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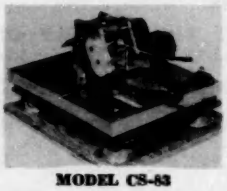

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The Influence of Weathering Prior to Harvest on Certain Properties of Cotton Fibers

P. B. Marsh, G. V. Merola, M. L. Butler, and M. E. Simpson

Crops Research Division, Agricultural Research Service, U. S. Dept. of Agriculture, Beltsville, Md.

Abstract

Most of the commercial cotton fiber produced in the United States is subjected to a period of from one to many weeks of exposure to the weather before it is harvested from the plant. Such weathering has been shown in prior work to be a cause of changes in the wax on the fiber [19], in the fiber's swelling behavior in alkali [22], and, under humid conditions, in the pH of water extracts of the fiber [21]. Subsequent investigation now has revealed that a number of other fiber properties also may undergo change during preharvest weathering. These properties include moisture regain at constant relative humidity, dye absorption, content of water-soluble reducing substances, browning tendency, rate of wetting in a water–alcohol mixture, length, strength, and susceptibility to enzymatic decomposition. As might have been expected, the X-ray angle, as defined by Berkley and co-workers [4], showed little if any alteration. Several of the fiber properties which change during weathering have been measured on commercial fiber samples and the results found to show a relationship to the grade of the fiber. Further work is in progress to analyze the nature of the above fiber property changes and to detect other changes which may occur. A rapid and practical test for measuring the water-soluble copper-reducing constituents in raw cotton fiber is described.

Introduction

When a cotton boll begins to open, it first cracks along certain well-defined sutures and then, provided there is adequate sunlight and dry conditions, it flares open within a few hours and the fiber dries. If, on the other hand, the weather is overcast and humid, or the boll is located in a damp situation under a canopy of leaves, microbial infection may take place at the cracking stage and the moist fiber may be severely damaged or even destroyed. Certain aspects of the problem of microbial damage at the time of boll opening have been presented in earlier papers [20, 21]. Even if a boll has opened normally, and without fiber deterioration, its fiber may still undergo alteration as a result of weathering influences during the period in the field before it is harvested. The present paper deals with fiber property changes during this postopening, preharvest period.

As a background for the data to be reported in the present paper, it seems worthwhile to mention briefly such information as is already available from prior work on the problem of property changes

which occur during preharvest weathering. While a thorough review of the available data is not attempted here, information in the references cited in the following paragraphs should be helpful to readers interested in a detailed analysis of the subject.

The pH of an aqueous extract of cotton fiber has been shown to increase rapidly and markedly during humid preharvest weathering [21]. When certain micro-organisms which had been found commonly on weathered cotton [17] were grown on the fiber in pure culture in the laboratory, a similar pH increase occurred [21]. As a result of this and other types of evidence, it was concluded that the pH change in fiber in the field is actually a response to microbial growth. The change is a very sensitive one and may occur before measurable alterations in any of several other properties. The fungi concerned are basically capable of causing strength loss in the fiber [18]. Because of its extreme simplicity, the pH test is well adapted to routine use. A general scheme for interpretation of pH results on raw cotton has been suggested [21]. Lower grades of cotton, especially from the humid areas of growth, tend to exhibit higher pH values than do the higher grades [25].

The degree of swelling of cotton fiber in alkali increases during weathering in the field, especially during humid weathering [22]. Although less rapid and striking than the pH change, this alteration is still a significant one. In this case also, incubation with micro-organisms in the laboratory causes a similar change in the property. A centrifuge–weight increase method for measuring alkali swelling has been described [22].

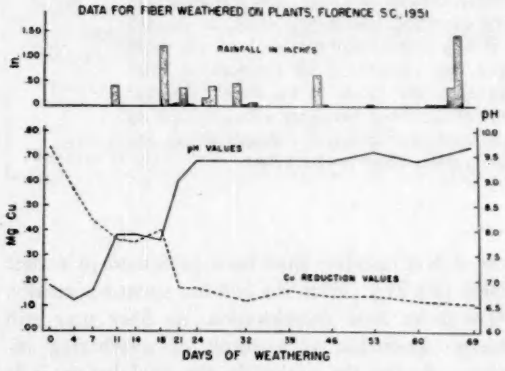

Fig. 1. Change in copper reduction value and aqueous extract pH of cotton fiber during humid preharvest weathering at Florence, South Carolina in 1951. Samples tested also for Pressley strength (1 mm. gap jaws) at each interval indicated in the graph, with resulting values of 4.75, 4.86, 4.92, 4.49, 4.46, 4.46, 4.48, 4.41, 4.48, 4.47, 4.60, 4.44, 4.32, and 4.50. Mean length decreased from 1.05 in. to 1.02 in. (See Table VI). Alkali centrifuge values increased from an original level of 202 to 215 at 24 days and to 233 and 237 at 32 and 69 days respectively.

The wax on a cotton fiber [19] undergoes a qualitative alteration during weathering which results in a lowering of its melting range and in an apparent increase in percent wax as measured by the Conrad method.

A darkening or graying in color of cotton fiber takes place during humid preharvest weathering. This darkening has been measured by Miss Nickerson [28] and is a strong determinant of grade. Proceeding from the writer's observations on microbial growth on fiber during preharvest weathering, Simon and Harmon [31] have attributed this color change directly to microbial action. Miss Nickerson [29] has noted that cotton which has turned gray during weathering has a decreased tendency to turn brownish during subsequent storage. A further contribution on this subject is reported in the present paper.

Data on the strength of cotton fiber as affected by weathering in the field is very limited. Using the Chandler bundle method on cotton weathered at three locations in Texas, Miss Grimes [6] found losses of 1–7% after 4–5 weeks of exposure, with average losses of approximately 8% after 13 weeks, 9% after 23 weeks, and 11% after 29–33 weeks. The degree of strength loss was not correlated with precipitation. Ultraviolet action was considered to be an important cause of strength loss. According to Hessler and coworkers [11] ". . . strength losses produced by weathering are negligible as measured by the Pressley tester . . ."; their data actually showed a fairly considerable degree of variability in strength from one sample to the next. Hawkins and Thomas [9] reported strengths of yarns spun from cotton weathered before harvest in Arizona for periods increasing to a maximum of 23 weeks. Calculations from their Table 3 indicate average strength changes per week of − 0.38%, − 0.36%, and − 0.73% as determined from their yarns strength figures for 22's, 36's, and 60's yarns respectively, or on the average for all yarn weights − 0.49%/week.

The mean length of cotton fiber has been found by Hessler and coworkers [12] to decrease approximately 0.04 in. during 2 months of preharvest weather exposure. These results, however, may well

be considered in conjunction with those of Hall and Elting [7], who have indicated that the length of high-pH cotton may decrease progressively during storage in the bale, thus suggesting the possibility of a type of delayed effect of humid weathering on the fiber.

Viscosity of cellulose from weathered cotton fiber has been measured by Hessler and coworkers [11, 13]. In one experiment the degree of polymerization, calculated from nitrocellulose viscosity, changed from approximately 10,400 to 8,500 during 43 days of sunny preharvest weathering.

Appearance under ultraviolet light was not found to be strikingly different for weathered cotton as compared with unweathered [26]. Certain brilliantly fluorescent spots were found in cotton from certain areas and shown to be a result of the growth on the fiber of the fungus *Aspergillus flavus* [26].

Experimental Results

Moisture Regain at Constant Relative Humidity

Moisture regain at a constant relative humidity is commonly regarded as an important property of cellulosic fibers. Numerous tests in our laboratory have pointed to the general conclusion that cotton fiber subjected to preharvest weathering before picking exhibits a lower moisture regain than cotton picked promptly after opening. Data on the point have been obtained principally at the unusually high relative humidity of 92%, which accentuates differences in moisture regain between different samples (Tables I and II). Confirmatory data showing lower but still regular differences also have been secured at the more conventional 65% relative humidity (Table I). Further data, on the 1954 crop, also showed similar trends. Thus, for exposure periods

TABLE 1. Effect of Preharvest Weathering in 1948 at Various Locations on Several Properties of Cotton Fiber *

Sample: location, variety, and period of weathering	Moisture regain at relative humidity		Copper reduction values	Alkali centrifuge values	Strength, Stelometer, ⅛ in. jaw gap	Elongation, Stelometer	Surface area (Arealometer)
	92%	65%					
Florence, S. C.							
Coker 100, none	16.2	7.1	.92	183	1.69	.50	403
Coker 100, 11 wk.	14.6	6.9	.06	245	1.52	.42	400
Deltapine 15, none	16.4	7.2	.57	184	1.80	.53	430
Deltapine 15, 11 wk.	14.0	6.7	.14	251	1.57	.48	450
Rowden 41 B, none	15.7	6.9	.49	175	1.69	.46	374
Rowden 41 B, 11 wk.	13.9	6.9	.17	231	1.51	.43	362
Jackson, Tenn.							
Coker 100, none	16.3	7.2	.73	197	1.63	.43	496
Coker 100, 10 wk.	14.9	6.9	.29	224	1.55	.39	514
Deltapine 15, none	16.8	7.6	.71	196	1.75	.45	488
Deltapine 15, 10 wk.	14.3	6.8	.25	233	1.57	.43	526
Shafter, Cal.							
Coker 100, none	16.7	7.4	.57	210	1.74	.41	501
Coker 100, 11 wk.	16.4	7.1	.53	236	1.53	.45	556
Deltapine 15, none	17.0	6.8	.41	206	1.68	.47	486
Deltapine 15, 11 wk.	15.9	6.6	.45	220	1.53	.44	512
Rowden 41 B, none	16.8	7.4	.45	187	1.62	.47	412
Rowden 41 B, 11 wk.	15.8	6.9	.45	196	1.45	.41	408
State College, N. M.							
Coker 100, none	17.7	7.4	1.29	194	1.63	.51	481
Coker 100, 12 wk.	15.6	7.0	1.11	218	1.46	.47	481
Deltapine 15, none	17.4	7.2	.99	196	1.66	.52	494
Deltapine 15, 12 wk.	15.4	6.6	.64	211	1.48	.48	473
Rowden 41 B, none	16.8	6.8	.85	178	1.58	.45	387
Rowden 41 B, 12 wk.	14.6	6.4	.41	203	1.42	.47	402

* Humid weathering at Florence and Jackson and dry weathering at Shafter and State College.

of 0, 1, 5, and 10 weeks, fiber weathered at Auburn, Alabama exhibited moisture regain values at 92% R.H. of 18.2, 16.7, 15.3, and 14.6; at State College, New Mexico, of 17.6, 16.2, 16.0, and 15.9; and at Shafter, California, of 17.1, 16.2, 15.0, and 15.8, respectively. The decrease in moisture regain was most pronounced during the first 2 weeks of exposure, approximately 2% (17.6% reduced on the average to 15.6%), whereas the change during the succeeding 8 weeks was smaller, averaging less than 1% (15.6% to 14.7%). This change occurred during either humid or dry weathering.

Although there were small differences in arealometer values between unweathered and weathered samples in Tables I and II, it was apparent that the moisture regain differences observed were actually independent of the fiber wall thickness as reflected in arealometer results. This situation was also evident in another series of moisture regain tests, which was carried out on unweathered cotton from a "zero fertilizer" plot at Florence, South Carolina. In these tests, fiber was taken from plants which had been grown on a plot to which no fertilizer had been added in 35 years. The bolls were extremely variable in size and the fiber showed wide variations in arealometer value from one boll to the next. With fibers exhibiting arealometer values of 438, 494, 502, 529, 530, 553, 564, 594, 598, 602, 628, 633, 634, 656, 664, 701, 708, 720, 748, 749, 753, 772, 791, 803, 812, 823, 840, 845, 897, and 922, the moisture regain values obtained were 16.2, 16.7, 17.9, 16.9, 16.9, 15.9, 16.7, 17.7, 16.5, 15.4, 16.4, 16.8, 16.9, 16.9, 17.6, 17.4, 16.4, 17.0, 16.0, 14.0, 16.0, 16.8, 16.9, 17.0, 15.4, 16.4, 16.0, 15.3, 16.5, and 16.5 respectively. The data thus failed to show any relationship between moisture regain and wall thickness.

Other workers have pointed out that the heating processes to which raw cotton may be subjected prior to ginning may cause a decrease in equilibrium moisture content [8, 15]. In respect to this matter it seems of importance to realize that the fiber as it comes from the field already exhibits considerable variability in this property, so that any differences resulting from heating are superimposed upon differ-

TABLE II. Effect of Preharvest Weathering on Properties of Cotton Fiber at Florence, South Carolina, 1951–54

Year of growth and length of preharvest weather exposure	Rainfall, cumulative, in.	Moisture regain (92% R.H.)	Dye absorption	Copper reduction values	pH values	Alkali centrifuge values	Surface area (Arealometer)
1951							
None	None	16.8	.35	.64	6.9	201	522
1 wk.	None	17.1	.36	.47	6.8	208	526
2 wk.	.40	16.1	.30	.38	7.9	208	503
5 wk.	2.99	14.5	.22	.18	9.4	231	501
10 wk.	5.52	14.4	.23	.16	9.7	237	528
1952							
None*	None	17.4	.48	.64	6.8	186	423
2 wk.	.65	14.8	.27	.20	8.4	223	438
5 wk.	1.47	14.5	.25	.13	9.5	249	423
10 wk.	1.47	13.9	.17	.14	8.9	271	416
1953							
None	None	18.3	.48	.72	7.0	189	451
1 wk.	.36	16.6	.35	.56	7.2	182	442
2 wk.	1.96	15.6	.26	.30	8.6	188	412
5 wk.	4.26	15.1	.27	.18	8.8	207	461
10 wk.	4.26	14.5	.19	.14	8.7	215	458
1954							
None	None	17.9	.35	1.12	6.8	185	446
1 wk.	None	15.9	.33	1.14	6.8	197	464
2 wk.	.14	15.7	.34	1.15	6.7	199	478
5 wk.	.84	14.8	.29	.47	8.2	200	470
10 wk.	6.84	14.0	.23	.46	7.7	221	490

* No 1-wk. sample available in this series.

ences already in the fiber. Hessler and Upton [13] observed no change in crystallinity of cotton fiber cellulose even after 133 days of weathering. It would appear that the iodine absorption method used in their work does not give results which parallel those obtained by the moisture equilibrium type of test here used.

Dye Absorption

When paired samples of unweathered and weathered raw cotton fiber were placed in a water solution of the direct dye Chlorantine Fast Green BLL, it was found that the amount of the dye removed by the fiber from the dye bath under the conditions used was lower for the weathered samples than for the unweathered ones (Table III). In most cases there was a clearly visible difference in the shade of the two paired samples, the unweathered sample appearing a deeper green. If the samples were alkali boiled or alkali boiled and bleached with hypochlorite prior to dyeing, the weathered samples still absorbed less dye than the unweathered, although the absolute amounts of dye absorption were increased for both unweathered and weathered fibers by these pretreatments (Table III).

When raw cotton samples, unweathered and weathered, were swollen in 18% NaOH prior to dyeing, the weathered samples frequently, but not invariably, absorbed more dye than the unweathered (Table III). This result apparently occurred in consequence of the higher degree of swelling of certain of the weathered samples in the 18% NaOH. Of the samples listed in Table III, only those from Florence exhibited a distinctly higher alkali cen-

TABLE III. Effect of Preharvest Weathering of Cotton Fiber in 1948 on Its Absorption of the Direct Dye Chlorantine Fast Green

Sample: location, variety, and period of weathering	Percent dye absorbed by fiber exposed to following treatments prior to dyeing					
	None	Alkali boiled	Alkali boiled, bleached	Swollen in 18% NaOH	Alkali boiled, swollen in 18% NaOH	Alkali boiled, bleached, swollen in 18% NaOH
Florence, S. C.						
Coker 100, none	.45	.64	.62	.58	.72	.72
Coker 100, 11 wk.	.33	.57	.60	.71	.79	.75
Deltapine 15, none	.45	.67	.60	.60	.70	.66
Deltapine 15, 11 wk.	.32	.58	.58	.75	.78	.74
Rowden 41 B, none	.44	.64	.58	.57	.69	.66
Rowden 41 B, 11 wk.	.28	.51	.51	.71	.76	.68
Jackson, Tenn.						
Coker 100, none	.59	.71	.62	.64	.77	.73
Coker 100, 10 wk.	.42	.64	.65	.69	.76	.80
Deltapine 15, none	.58	.72	.70	.68	.75	.78
Deltapine 15, 10 wk.	.45	.72	.65	.73	.75	.80
Shafter, Cal.						
Coker 100, none	.58	.70	.64	.65	.74	.74
Coker 100, 11 wk.	.48	.67	.62	.68	.72	.72
Deltapine 15, none	.57	.74	.69	.70	.74	.72
Deltapine 15, 11 wk.	.42	.64	.62	.62	.72	.67
Rowden 41 B, none	.53	.67	.65	.60	.72	.72
Rowden 41 B, 11 wk.	.40	.59	.59	.58	.67	.67
State College, N. M.						
Coker 100, none	.62	.69	.64	.62	.80	.74
Coker 100, 12 wk.	.36	.58	.60	.67	.75	.75
Deltapine 15, none	.65	.76	.67	.64	.82	.73
Deltapine 15, 12 wk.	.42	.59	.57	.64	.73	.71
Rowden 41 B, none	.50	.63	.59	.55	.74	.65
Rowden 41 B, 12 wk.	.35	.54	.51	.60	.72	.68

trifuge value for the weathered than the corresponding unweathered fiber. If alkali boiling or alkali boiling and bleaching preceded the alkali swelling, the differences in dye absorption between unweathered and weathered samples tended to be minimized (Table III). The higher dye absorption of weathered mercerized as compared with unweathered mercerized fiber is paralleled by the behavior of fiber incubated in a saturated atmosphere with *Cladosporium*. Thus, fiber incubated for periods of 0, 4, 7, 14, 21, and 28 days, swollen in 18% NaOH, and dyed, show dye contents after 1 hr. of 0.55, 0.56, 0.63, 0.71, 0.72, and 0.74%, respectively. The dye absorption by raw fiber decreases rapidly with weather exposure. It may be noted in Table II that in 1952–53 at Florence 2 weeks of weathering produced a marked decrease in dye absorption.

Leitgeb and Wakeman [15] and Hart and coworkers [8] have made the point that heating at the gin decreases dye absorption by cotton fibers. As with moisture regain, it may be worth noting that differences in dye absorption brought about by heat are superimposed upon differences already present in the fiber at the time of harvest.

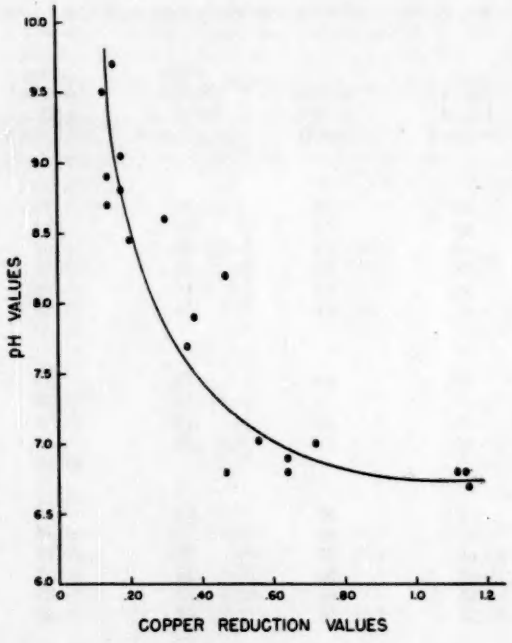

Fig. 2. Aqueous extract pH and copper reduction values for cotton fiber weathered at Florence, South Carolina, 1951–54, plotted to show relationship of the two properties. In accord with these observations were many additional tests on raw cotton samples of unknown history, in which high pH values were regularly accompanied by low copper reduction values.

Copper Reduction Values and Browning Capacity

Cotton fiber exposed to humid weathering prior to harvest exhibited a decrease in the level of reducing constituents present, as measured by a copper reduction technique (Tables I and II and Figure 1). The effect is mainly concerned with water-soluble materials, probably mostly sugars. While this change may be due in part to leaching of the fiber by rain, it seems highly probable that the main cause is usually the utilization of sugars by micro-organisms growing on the fiber. This conclusion is supported by the fact that decreases in copper reduction values are readily produced by growing microorganisms on the fiber in the laboratory [24]. Furthermore, in field-weathered samples, as in laboratory-incubated ones [24], a relationship is observed between copper reduction values and pH values, humid exposures leading in both cases to high pH along with the low copper reduction values (Table II). Data illustrating this relationship, as seen with fiber weathered during four successive years (1951–1954 inclusive) at Florence, South Carolina, are shown in Figure 2. Data for changes with time during a single weather exposure are shown in Figure 1. Water-leaching of fiber leads, of course, to a decrease in copper reduction value but not to an increase in pH [21].

With several agricultural products other than cotton it has been noted by other workers that the tendency toward browning is associated with sugars [14]. Since humid weathering produced a decrease in copper reduction value, it was thought that possibly a decrease in browning tendency might also occur in such samples. This was, in fact, found to be the case. Thus, samples from Florence, South Carolina weathered for 0, 5, and 10 weeks in 1953 exhibited brownness increases during heating at 160° C. for 10 min. of 3.9, 2.6, and 2.2; similarly, 4.6, 3.9, and 2.9 for 1954 samples. Copper reduction values on these samples may be seen in Table II. Samples weathered at Auburn, Ala. 0, 5, and 10 weeks in 1954 showed brownness increases under the same circumstances of 4.0, 3.2, and 2.4, along with copper reduction values of 0.79, 0.37, and 0.42 and pH values of 6.7, 8.7, and 8.9. Samples weath-

ered at Shafter, California in 1954 showed little change in copper reduction value (0.60, 0.64, and 0.50) and no decrease in brownness induced by heating (3.9, 4.3, and 4.3). Commercial fiber samples heated at 160° C. also showed a similar relationship of copper reduction value to browning tendency (Figure 3). In these samples the pH and the copper reduction value were known before heating; it may be noted from the figure that the high-pH samples had low copper reduction values and exhibited a low degree of browning. The browning tendency may also be decreased by simply washing water-soluble materials out of the fiber with water.

With a series of classer's samples stored for a period of 2 yr. at room temperature, the increase in brownness which occurred was correlated in an approximate fashion with the copper reduction value prior to storage (Figure 4). These results are in accord with the data obtained by Nickerson [28], who noted less browning in storage with weathered samples. It is apparent that the decreased browning tendency in storage is associated with a history of humid weathering.

Although one might be tempted to conclude from the above evidence that the browning of cotton fiber is related directly to changes in the content of reducing sugars present, this is by no means necessarily a complete analysis of the matter, because certain organic acids (malic, citric, and others) are also found in unweathered fiber and are also known to undergo browning. Further, McCall and others [27] showed that high-pH weathered cotton is lower in organic acid content than unweathered fiber. Additional work on the browning reaction in cotton fiber is currently underway in the writers' laboratory.

Alkali Centrifuge Values

As has been reported before [22], the alkali centrifuge value is a combined index reflecting both the thickness of the fiber's secondary wall and the occurrence of damage in the outer wall. Consequently, a diagnosis of fiber damage must be based upon both an arealometer value (or some other index of wall thickness) and an alkali centrifuge value. If the data in Table I for alkali centrifuge value and arealometer value are plotted against each other, it becomes apparent that for weathered fiber the alkali centrifuge value is higher for any level of arealometer value than is the case for unweathered fiber. Thus for the three weathered samples from Florence in Table I, the alkali centrifuge value is more than 60 points in excess of the same for undamaged fiber of corresponding arealometer value. When fiber is damaged by microbial action in the "tight lock" condition, alkali centrifuge values increase even more markedly; Figure 5 illustrates this fact. The points

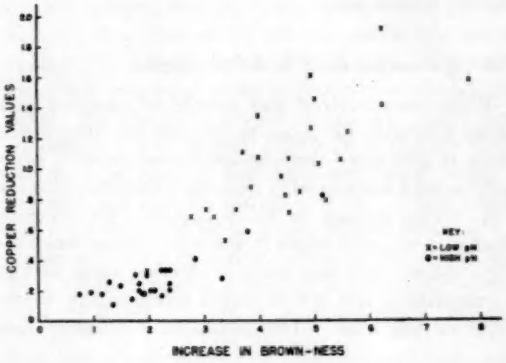

Fig. 3. Increase in brownness of commercial cotton fiber samples during heating at 160° C. for 10 min. in comparison with the copper reduction (CR) values of the same fiber. Note that the greatest browning accompanied highest CR values, also that high-pH samples (pH 8.0 or higher) browned less than low pH samples (pH 6.0–7.0). Samples came from all areas of the U. S. Cotton Belt.

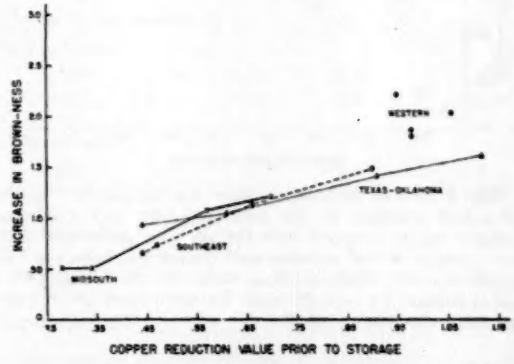

Fig. 4. Increase in brownness of commercial cotton fiber samples from each of four different areas of production during two years of storage at room temperature in relation to the copper reduction value of the samples prior to storage. Each point in the graph represents an average of 25 determinations on a single grade of fiber—Low Middling, Strict Low Middling, Middling, and Strict Middling—in order from left to right along each line in the graph. The Western samples had pH values in the range of 6.4–6.8 and therefore had not been subjected to humid weathering (Table X).

represented by ● correspond to undamaged fiber, whereas the points represented by x represented fiber damaged in the microbial "tight lock" condition. In work of this type it is convenient to run the arealometer determination first and then simply use the arealometer plugs for determination of alkali centrifuge value, thus avoiding the sampling error encountered if two separate samples are used for the two determinations.

Rate of Wetting in 50% Ethyl Alcohol

When unweathered and weathered samples were being prepared for aqueous extract pH determinations, it was noted that the weathered samples regularly wetted more quickly than the unweathered ones. This result seemed to be in accord with previous observations on changes in the wax during weathering. An attempt was made to develop some sort of a quantitative test which would relate to the wettability of the fiber. The technique eventually employed consisted simply of placing a 500-mg. sample of fiber on the surface of a 50–50 mixture of ethyl alcohol and water (200 cc. in a 250-cc. beaker) and measuring with a stopwatch the time required for the sample to become completely submerged. The samples were prepared in either of two ways; in loose wads or rolled into tight rolls of 18–20 mm. length and 14–16 mm. diameter, kept in a test tube prior to the test. Data obtained by this method may be seen in Table IV. Not only weathering but also heating causes changes in the submergence time in this test. Thus, unheated unweathered samples of Acala 4-42 and Deltapine 15 in wads had a submergence time of 76 and 62 sec. respectively, while the same samples after heating for 10 min. at 160° C. both yielded values of 5 sec. Samples prepared in rolls exhibited a similar response to heating.

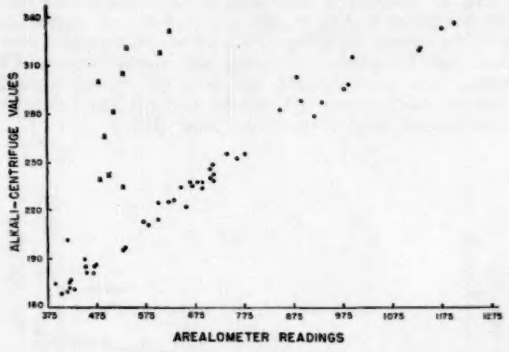

Fig. 5. Alkali centrifuge values and arealometer values on cotton damaged in the microbial tight lock condition (symbol x) as compared with the same for undamaged cotton (symbol ●) of varying wall thickness. Note the exceptionally high alkali centrifuge values for the damaged cotton in comparison with the same for undamaged cotton with the same arealometer value.

Fiber Strength

Methods for determination of strength of raw cotton have been for some time and still are a subject of debate and discussion. The Pressley method has been used extensively by cotton breeders and others and was employed in this investigation in numerous comparative tests on weathered and unweathered fibers. The conclusions which may be derived from the tests conducted are somewhat limited by the fact that relatively slight alterations in the method give rise to quite distinct differences in the results obtained. This circumstance is illustrated by the data of Table V, where it is seen that a variation in the speed of the car (as brought about by a slight change in the balance of the instrument) shifted the station-average loss in breaking strength, as did also the use of jaws with a 1-mm. gap in place of the usual "zero gap" jaws. In general, however, the results in Table V showed a loss averaging rather less than 1% of the original strength lost per week of weathering. It is not known that the use of some other method for strength determina-

TABLE IV. Effect of Preharvest Weathering on Submergence Time of Raw Cotton in a Water-Alcohol Mixture and Effect of Shape of Sample—1954 Crop Samples, 10-Wk. Weathering

	Submergence time, sec.			
	Samples in wads		Samples in rolls	
Location	Unweathered	Weathered	Unweathered	Weathered
Auburn, Ala.	61	29	9	5
Florence, S. C.	198	25	20	6
Shafter, Cal.	96	39	12	8

tion might not have resulted in either higher or lower losses.

In Table I strength values obtained by the use of the "Stelometer" of Dr. K. L. Hertel with a 1/8-in. breaking span are shown; these were provided by Dr. Hertel. Also in the same table are values for elongation as determined on the Stelometer. The tendency for weathered samples to exhibit decreased elongation at break may be noted.

Fiber Length

Numerous length determinations have been carried out on unweathered and weathered samples with the Suter-Webb sorter. Attention is directed first to the data of Table V, where it is seen that in spite of large differences in amount of rainfall, the Florence and Shafter samples averaged almost the same in length loss. These results suggest that sunlight may be quite as effective as humid weather exposure in causing decreases in fiber length. Data in Table VI showed a loss of only 0.03 in. during weathering for approximately 10 weeks at Florence, South Carolina, in 1951. Similarly, cotton weathered 10 weeks prior to harvest at Florence in 1953 showed only a 0.02-in. loss in length.

It has been the experience of Hall and Elting [7] that the Suter-Webb mean length of certain high-pH samples decreases during storage of the fiber. To further investigate this interesting point, several samples of cotton weathered for different time periods at Florence in 1951 and exhibiting widely differing pH values were tested on the Suter-Webb sorter before and during a period of storage under room conditions. The results (Table VI) did not bring out the occurrence of any consistent loss in length of the high-pH samples during storage. These results are not considered to be necessarily contradictory to those of Hall and Elting, whose experiments may have differed in some unknown way from the experiment of Table VI, but it certainly seems true that

TABLE V. Effect of Weathering Approximately 11 Weeks in the Field Prior to Harvest at Florence, S. C. and at Shafter, Cal. in 1948 on Strength and Length of Cotton Fiber—Total Rainfall of 15.0 In. at Florence and 0.34 In. at Shafter

Sample	Varieties								Average change, all varieties
	Acala 1517	Acala 4-42	Coker 100	Coker Wilds	Deltapine	Mebane	Rowden	Stoneville 2B	
	Pressley strength: percent change during weathering								
	Zero gap jaws, fast car speed								
Florence	−5.0*	−9.3**	−9.1**	−11.2**	−7.6**	−6.7**	−6.9	−0.40	−7.5
Shafter	−1.3	+1.1	−6.9*	−3.2	−7.7*	−3.0	−0.6	−1.6	−2.9
	Zero gap jaws, slow car speed								
Florence	−3.3	−6.8**	−5.7*	−1.8	−3.2	−7.3**	−6.5**	−2.8	−4.7
Shafter	−1.9	−7.0**	−5.9*	−6.6**	−5.9*	−6.0**	−4.2*	−1.6	−4.9
	1-mm gap jaws, slow car speed								
Florence	−2.9	−3.5	−6.1*	−5.1*	−9.1**	−12.4**	−7.2**	+0.9	−5.9
Shafter	−4.9**	−12.1**	−10.3**	−9.5**	−12.0**	−9.5**	−11.3**	−12.7**	−10.3
	Mean length, Suter-Webb, in. †								
Florence, unweathered	.92	.92	.91	1.09	.89	.85	.85	.92	
Florence, weathered	.89	.92	.84	1.00	.80	.79	.82	.80	−.061
Shafter, unweathered	1.00	.92	.93	1.14	.94	.88	.90	.92	
Shafter, weathered	.94	.92	.91	1.02	.92	.80	.87	.84	−.051

* Denotes a significant mean difference at 0.01 level.

** Denotes a significant difference at 0.05 level. Each figure an average derived from 10 breaks.

† Each figure is a mean of duplicate determinations, the average deviation of the individual values from this mean for all pairs being 0.009 in.

not all high-pH samples lose length under all conditions of storage.

Yarn Strength

When samples of unweathered and weathered fiber were spun, the yarn strength losses associated with weathering amounted on the average to about 0.8% strength loss per week of weathering (Table VII). There was variation in the amount of loss in different locations and years. The two locations showing greatest yarn strength losses, Shafter and Stoneville (1949), also showed the highest Pressley strength losses. Since a period of 10 weeks of preharvest weathering is by no means unusual in commercial cotton operations, it is obvious that the yarn strength losses which may be associated with preharvest weathering are often of real practical significance. It also seems apparent that the losses are large enough, in general, to indicate that in tests on experimental cottons differences in degree of weathering between different test samples may require attention in interpreting results.

TABLE VI. Mean Length by the Suter-Webb Technique and Aqueous Extract pH of Fiber of the Variety Coker 100 Exposed to Weathering Prior to Harvest in 1951 and Tested in January 1952 and at Intervals Thereafter

Date of determination	Values obtained on samples harvested on:				
	8/27/51	9/7/51	9/20/51	10/12/51	11/4/51
	Mean length in inches				
Jan. 1952	1.05	1.00	1.02	1.00	1.02
Apr. 1952	1.08	1.04	0.98	0.99	1.00
July 1952	1.05	1.03	1.02	1.00	0.97
Oct. 1952	1.03	1.00	1.02	0.94	1.00
Oct. 1953	1.07	1.00	0.99	0.98	1.02
	Aqueous extract pH				
Jan. 1952	6.9	7.9	9.4	9.4	9.7
Apr. 1952	6.4	7.0	7.5	7.7	8.2
July 1952	6.7	7.2	7.9	7.8	8.0
Oct. 1952	6.5	6.8	7.2	7.3	7.5
Oct. 1953	6.5	7.1	7.4	7.6	7.8

Susceptibility to Enzymatic Decomposition

Abrams [1] has reported that cotton fabric exposed to weathering becomes more resistant to strength loss during subsequent incubation with the fungus *Chaetomium globosum*. These results suggested the possibility that cotton fiber exposed to preharvest weathering might be less susceptible to attack by the enzyme cellulase than unweathered fiber. Under conditions here described, this has turned out to be the case. The experimental evidence may be described as follows.

A solution containing the enzyme cellulase was prepared by growth of the fungus *Myrothecium verrucaria* on raw cotton fiber as previously described [23]. Cotton fiber was then placed into a solution of this enzyme and shaken on a mechanical shaker. In a short time many fibers broke up into fragments, and the degree of fragmentation was measured by simply washing out the short pieces from the main fiber mass with a stream of water and then drying and weighing the latter, the results being expressed in terms of percentage by weight of the fiber lost by fragmentation. When experiments of this type were carried out on 10-week weathered and unweathered

TABLE VII. Effect of Preharvest Weathering of Cotton on Pressley Strength and on the Strength of Yarns Made from the Fiber—Tests Performed by the USDA Spinning Laboratory at College Station, Texas

Location and year of exposure	Length of exposure period, wk.	Percent change per wk.*			
		Pressley strength	Yarn strength		
			22's	36's	50's
Shafter, Cal. (1949)	9½	−.84	−1.17	−0.93	−1.03
State College, N. M. (1949)	11	−.27	−0.52	−0.61	−0.61
Stoneville, Miss. (1949)	11½	−.37	−1.36	−1.22	−1.10
Experiment, Ga. (1950)	10	0.0	−0.55	−0.82	−0.67
Stoneville, Miss. (1950)	9½	−.02	−0.50	−0.53	−0.37
Average percent change in strength, all locations, both years		−.30	−0.82	−0.82	−0.76

* Each figure in the table is based on an average from tests on two cotton varieties as follows: Shafter, Cal. (1949)—Deltapine 15 and Acala 4-42; State College, N. M. (1949)—Coker Wilds and Acala 1517W; Stoneville, Miss. (1949)—Stoneville 2B and Delfos 4313; Experiment, Ga. (1950)—Coker 100W and Empire; Stoneville, Miss. (1950)—Deltapine and Delfos 7272.

cotton fiber, it was found that the weathered fiber was less susceptible to fragmentation (Table VIII).

X-Ray Diffraction Pattern

In the breeding of new cotton varieties, much attention has been paid to the X-ray angle of the fiber, as defined and determined by Berkley and coworkers [4]. Since the samples so tested in this breeding program have often been subjected to differing and unknown periods of preharvest weathering prior to testing, it was considered of importance to know whether or not such weather exposure affected the X-ray angle. There seemed to be no *a priori* reason to expect a change, but the point was of such considerable practical importance in connection with the breeding work that a check was made on it (Table IX). The tests were run on the same samples shown in Table V. The average for all varieties of the Florence samples before weathering was 37.9; for the weathered samples from the same location the average was 37.4. For the Shafter samples the average for all varieties before weathering was 37.8; for the weathered samples from the same location the average was 36.6. From the data contained in Table IX it may be seen that weathering resulted in very little, if any, alteration in the X-ray angle.

Weathering Effects in Relation to Grade of Fiber

Since weathering in the field before harvesting in many cases influences the classer's grade, it might be suspected that at least in some cases the lower-grade samples would show fiber properties characteristic of weathered cotton. Some degree of variability in the relationship between grade and fiber properties would necessarily be expected, since the grade may be influenced by the amount of leaf trash in the sample, the excellence of preparation, and other factors not having to do with weathering. In the present work certain relationships between grade and fiber properties have, in fact, been observed to exist.

In tests on classer's samples from the 1954 United States crop, it has been found that a correlation exists between pH and grade, the preponderance of high-pH samples being in the lower grades [25]. Even in the Middling White grade, however, about 10% of the samples were found to have a pH of 8.0 or higher, this situation being considered to be simply a result of the very high sensitivity of the pH response to microbial growth.

Table X presents data on moisture regain, dye absorption, copper reduction value, and pH for a series of 400 samples from the crop of 1954. Each figure in the table represents an average of results on 25 samples from a particular grade of fiber from one of the four major geographical areas represented. It will be noted that for three of the areas (Southeast, Mid-South, and Texas-Oklahoma) a rather clear trend of relationship between each fiber property and the grade was found, although in the Western area such trends were absent. It is considered

TABLE VIII. Effect of Preharvest Weathering on the Fragmentation of Cotton Fiber in a Cellulase-Containing Filtrate from the Growth of the Fungus *Myrothecium verrucaria*

Fiber sample: source and year of growth*	Percent weight loss due to fragmentation	
	Unweathered	Weathered
Florence, S. C., 1951	21.0	11.0
Florence, S. C., 1952	19.0	10.0
Florence, S. C., 1953	22.0	12.0
Florence, S. C., 1954	19.2	11.0

* Variety: Coker 100 W

TABLE IX. X-Ray Angle of Unweathered Cotton Fiber of Eight Varieties Grown at Florence, S. C. and Shafter, Cal. in 1948 and Also of Fiber of the Same Varieties After 10 Weeks of Weathering

Location and variety	X-ray angle	
	Unweathered	Weathered
Florence, S. C.		
Acala 4–42	36.9	34.8
Acala 1517	34.0	32.6
Coker Wilds	36.2	37.6
Coker 100W	38.2	40.4
Deltapine 15	39.3	38.8
Mebane (Watsons)	44.6	45.0
Rowden 41B	37.8	35.8
Stoneville 2B	36.2	34.6
Average	37.9	37.4
Shafter, Cal.		
Acala 4–42	32.0	34.3
Acala 1517	33.6	31.4
Coker Wilds	36.2	35.6
Coker 100W	40.0	38.2
Deltapine 15	41.4	38.3
Mebane (Watsons)	43.6	41.2
Rowden 41B	39.4	39.7
Stoneville 2B	36.2	34.2
Average	37.8	36.6

that in the Western area the grade designation represented principally an index of the amount of leaf trash in the sample rather than a condition of the fiber and that the lack of grade–fiber property relationship consequently is not surprising.

Discussion

The copper reduction test here described is a method worked out in this laboratory after consideration of numerous alternative variations. It is simple, safe, and inexpensive to perform and adapted to routine use. It should not be confused with any of the various "copper number" determinations which are used frequently on cotton cellulose [30]. The latter type of determination is carried out on fiber from which the water-soluble fraction has been removed, and is designed to measure the degree of cellulose degradation in terms of the reducing power of the cellulose itself. The test here described, on the other hand, is carried out on raw, unextracted fiber, and quantitative differences among samples of the type here used reflect almost entirely differences in the amount of copper-reducing water-soluble material present. Thus, for example, when three pairs of samples of unweathered and weathered cotton were thoroughly extracted with warm water and then run in the CR test, all samples yielded CR values between 0.05 and 0.08, whereas values on the unextracted fiber ranged from 0.27 to 1.16. The CR test differs from most other copper reduction methods in the incorporation of an indirect iodometric determination for the reduced copper. Other methods for a similar purpose include the ESRM procedure of Hall and Elting [7] and a picric acid method described from this laboratory [24], both methods being somewhat more rapid and less accurate than the CR test.

TABLE X. Relation of Four Fiber Properties to Grade in Commercial Cotton of the 1954 Crop

Grade	Southeast	Mid-South	Texas-Oklahoma	Western
	Moisture regain			
Strict Middling	16.6	15.8	16.7	17.0
Middling	16.5	15.3	16.0	16.5
Strict Low Middling	15.5	14.8	15.8	16.7
Low Middling	15.4	14.9	15.5	17.0
	Dye absorption			
Strict Middling	.39	.34	.43	.41
Middling	.38	.33	.40	.40
Strict Low Middling	.27	.26	.36	.37
Low Middling	.27	.24	.33	.42
	Copper reduction values			
Strict Middling	.90	.70	1.12	.95
Middling	.66	.57	.91	.98
Strict Low Middling	.46	.34	.61	1.06
Low Middling	.44	.28	.44	.98
	Aqueous extract pH			
Strict Middling	6.4	6.8	6.4	6.4
Middling	6.8	6.8	6.4	6.4
Strict Low Middling	7.5	8.2	6.8	6.4
Low Middling	7.5	8.6	7.2	6.8

In recent years spinners and other processors of cotton frequently have complained that the fiber now available in commercial channels is in some way or other less desirable or less easily processed than was the case with cotton produced some years ago. Ends down, excessive fly, low yarn strength, poor dyeing performance, and other problems have been mentioned, and various factors have been claimed by one or another individual to be sources of these difficulties. New varieties, new cultural practices, microbial damage to the fiber, aphid honey-dew, mechanical harvesting, damp storage of seed cotton, excessive heating at the gin, and rough cleaning practices all have been discussed among cotton workers in this connection. Federal and State employees engaged in work with cotton generally have regarded these problems with concern and are moving in cooperation with each other and with farmers and cotton processors in the direction of their definition and solution. It is recognized generally that many variable factors may influence the processing performance of any particular sample of cotton, but more exact and detailed knowledge is needed concerning the nature of these variables, methods for measuring them, and methods for preventing, avoiding, or alleviating their influences. The several weather-influenced variables discussed in the present paper all seem to require further experimental analysis before their theoretical and practical significance may be entirely understood. Nevertheless, it is felt that a worthwhile degree of progress has already been made with this problem.

Individuals carrying out spinning or other processing operations on cotton are sometimes confronted with the situation that a certain lot of cotton exhibits poor behavior in processing for some unknown reason. Not infrequently very little is known about the history of cotton which causes difficulty, and it would be highly desirable to have at hand some quick diag-

nostic methods by which the fiber could be tested and the cause of the difficulty determined. Although the methods currently available do not seem to the writers to be adequate to accomplish this objective with certainty in more than a fraction of the cases of difficulty, still it may be useful to try to define what types of diagnostic information may be arrived at with the methods now available. The following types of test results seem to the writers to have some utility in this respect.

High aqueous extract pH. All presently available data indicate that with samples having a pH of 7.5 or higher, one may conclude that the fiber has undergone a period of exposure to humid conditions and has supported at least a small amount of microbial growth. Frequently the humid exposure took place in the field prior to harvest, and in some of these cases the wet weather occurred at a time when some of the bolls were in the process of opening; these latter bolls suffered severe microbial damage in the tight lock condition. Thus, a high pH does not indicate with certainty the existence of fiber from microbial tight locks in the bale, but does suggest the possibility of it. Cotton stored in a damp condition subsequent to harvest would also, of course, develop a high pH as a result of microbial action.

Cotton of high pH very regularly is observed to have a low copper reduction value; this seems to accompany a low tendency to turn brown either in storage or under the influence of heat.

High copper reduction value. Results as presented in this paper point to the conclusion that cotton with a high copper reduction value is likely to exhibit a greater tendency to turn brown in storage than fiber with a lower value. It is recognized that the relationship between these two properties may be a rather indirect one. However, malic acid is present in fair quantity in cotton fiber; it does not affect the copper reduction value, but does have a distinct tendency to turn brown under some conditions. Possibly there is a general parallelism between reducing constituents and organic acids in the fiber.

Low moisture regain at 92% relative humidity. Cotton fiber at a time shortly after the first opening of the bolls and drying of the fiber has a moisture regain at 92% relative humidity in the range of 15.7–18.3%, whereas fiber weathered prior to harvest has been observed with moisture regain in the range of 13.9–17.1%. Heating is also known to lower the fiber's moisture regain. It is presumed that fiber of unknown history which has a regain of less than about 15.7% has been either weathered or heated.

Bright greenish-yellow fluorescent spots. Bright greenish-yellow spots are sometimes observed under ultraviolet light in cotton from Texas, Oklahoma, Arizona, and California. It has been noted that fiber in such spots is weakened as a result of attack by the fungus *Aspergillus flavus* and exhibits a high degree of swelling in alkali. Many other fungi capable of injury to cotton are known to be nonfluorescent; it is assumed that a sample of cotton containing bright greenish-yellow fluorescent spots may also have other areas, not visible under the ultraviolet lamp, which also have suffered microbial damage. The certainty with which this interpretation may be made is limited by a lack of knowledge of the field conditions under which *A. flavus* infection occurs, but for the present at least the writers are inclined to view with suspicion any cotton which contains a considerable number of bright greenish-yellow fluorescent spots.

High alkali centrifuge value. Either a thin secondary wall or damage to the fiber's outer wall will lead to a high alkali centrifuge value. It is suggested that a high ratio of alkali centrifuge value to arealometer value (or to some other air-flow index) indicates fiber damage.

Helical splitting. Helical splitting seems to be particularly characteristic of cotton fiber acted upon by micro-organisms or microbial enzymes before the fiber has undergone initial drying at the time of boll opening. Photomicrographs illustrating this type of breakdown as seen under the microscope have been presented [16].

Rapid wetting in 50% ethyl alcohol. This test, as described below, is not sufficiently standardized for a precise definition of a routine procedure. Nevertheless, it seems worth mentioning that either weathering (dry or humid) or heating will cause the occurrence of rapid wetting in the water–alcohol mixture.

Conclusions

The following cotton fiber properties have been shown by data reported here to change during a period of weathering between the time of boll opening and harvest.

1. Moisture regain values decreased (dry or humid weathering).

2. Dye absorption decreased (raw, alkali boiled, or alkali boiled and bleached fiber) or increased (alkali swollen fiber with elevated alkali swelling values).

3. Copper reduction values decreased rapidly and markedly during humid weathering.

4. Browning tendency of the fiber during heating decreased as a result of humid weathering.

5. Aqueous extract pH increased rapidly and markedly during humid exposures (confirmation of previous data [21]).

6. Alkali centrifuge values increased.

7. Rate of wetting in 50% ethyl alcohol increased.

8. Pressley strength decreased during either humid or dry weathering.

9. Mean fiber length (Suter-Webb) decreased about 0.02–0.05 in. for 10 weeks weathering, with no indication of continued loss in length during subsequent storage of high-pH samples.

10. Yarn strength decreased, losses being variable but averaging about 0.8% of the original strength per week of weathering.

11. Susceptibility to enzymatic decomposition, as measured with a cellulase-containing filtrate from the growth of a fungus, decreased.

The X-ray angle, as defined by Berkeley [4], showed no change during weathering.

With samples from Southeastern, Mid-South, and Texas-Oklahoma growing areas, there was a relationship between grade of sample and each of five properties—moisture regain, dye absorption, copper reduction values, browning tendency during storage, and aqueous extract pH. With Western (California) samples, none of these properties exhibited a relationship to the grade of the fiber, the grade in these samples apparently being principally determined by the amount of trash present or some other property not directly related to properties of the fiber.

A rapid and practical new copper reduction test, applicable to raw, unextracted cotton fiber, with results reflecting the amount of water soluble reducing constituents in the fiber, is described.

A brief summary of prior data on effects of preharvest weathering on cotton fiber properties is presented.

Acknowledgments

The work here reported was carried out under the general scientific direction of Drs. Thomas Kerr and H. D. Barker, to both of whom the authors express their thanks for helpful comments and advice during the progress of the investigation.

The authors wish to acknowledge with thanks the kindness of Miss Dorothy Nickerson in carrying out the color determinations reported in this paper and in providing the samples of commercial cotton fiber used.

Appendix—Methods

The methods used in the work reported in the present paper were as follows.

Moisture Regain at Constant Relative Humidity

Moisture regain determinations at 92% relative humidity were carried out as follows. Place approximately 0.500 g. of fiber on glass support bars over a saturated solution of sodium bromate, $NaBrO_3$, in 500-cc. French square bottles, the solution previously having been brought to equilibrium in a room maintained at 20° C. After 7 days, remove samples individually from the 500-cc. bottles, place each quickly into a 20-cc. tall-form Pyrex weighing bottle of known weight. Weigh each bottle and sample on a standard chemical analytical balance. Dry sample in bottle in oven at 110–115° C. overnight, cool in desiccator, and reweigh. Calculate percent moisture in sample on basis of oven-dry weight of the fiber. Determination of aqueous extract pH on several of the samples following the moisture equilibrium and drying showed no indication of microbial growth on the fiber. A shorter equilibrium period would probably suffice.

Moisture regain determinations at 65% R.H. were carried out in the same manner, except that a saturated solution of sodium nitrite, $NaNO_2$, was used to obtain the desired humidity.

Dye Absorption

The dye was a sample of Chlorantine Fast Green BLL from Ciba, Inc. The fiber sample, weighing 500 mg., was first wet for 10 min. in a 0.05% solution of Aerosol, then excess water blotted off with a clean towel. The fiber was then dyed for 1 hr. at 80° C. in 25 cc. of dye solution in a 25 × 200 mm.

test tube containing 0.02% dye, supplemented with 0.02% sodium sulfate in tests on alkali swollen fiber and with 0.2% sodium sulfate in tests on non-alkali swollen fiber. The amount of dye absorbed was measured by determining the amount of dye remaining in the solution. A 1-cc. aliquot was removed from the dye solution, diluted to 10 cc. with water, and the dye concentration read on a Klett photoelectric colorimeter, using a 600 filter. The data are recorded in percentage of dye on the fiber. The alkali boiling which preceded certain dyeings was carried out by autoclaving the fiber at 15 lb. of steam pressure in 50 volumes of 1% NaOH for 5 hr. The bleaching was done with sodium hypochlorite at room temperature, using 50 volumes of NaOCl of 0.1% available chlorine for 1 hr.

Copper Reduction Test

The copper reduction test was carried out as follows. Weigh a 0.50-g. cotton sample into a test tube (25 × 200 mm.). Add 10 cc. of a copper reagent, of composition noted below, and 10 cc. of 0.05% Aerosol–water solution. Aerosol is a wetting agent (dioctyl sodium sulfosuccinate). Tamp and stir with a glass rod with flattened tip and spread out the fiber in the solution. Cover test tube with a "teardrop," glass marble, or other suitable air condenser and place into a glycerine-containing constant temperature bath at 85° C. Solution level in the test tube should be about 1 in. below the level of the liquid in the bath. Tamp and stir again after 15 min. After a total period of 45 min. at 85° C., remove tube and cool to room temperature by immersion in water. Swab down walls of test tube with cotton sample by means of glass rod. Then tamp sample. Pipette out exactly 10 cc. of the solution into a 125-cc. Erlenmeyer flask containing 2 g. of KI; allow to dissolve. Add 2 cc. of 4 *N* H_2SO_4. Shake vigorously until release of CO_2 subsides, then titrate with 0.005 *N* sodium thiosulfate until solution becomes a pale yellow. Let stand about a minute. Add 1–2 cc. starch indicator solution and titrate until solution remains colorless for 5 min. Run a blank, without sample, as above.

The copper reagent has the following composition: Na_2CO_3, 25.0 g.; Rochelle salts, 25.0 g.; $CuSO_4 \cdot 5\,H_2O$, 8.0 g.; $NaHCO_3$, 20.0 g.; and KI, 1.0 g. To prepare the reagent, add the Na_2CO_3 to about 600 cc. of distilled water in a 1-l. beaker. Stir until dissolved. Then add other reagents in the order listed, as each dissolves adding the next. Boil very gently for 2 min. (caution: bumping). Transfer to a 1-l. volumetric flask; rinse beaker four times with 100-cc. portions of distilled water. Let solution stand overnight. Adjust to liter mark and filter through a fritted glass filter. Store in a Pyrex bottle.

The sodium thiosulfate is standardized by the use of KIO_3. It is first standardized at approximately *N*/10, stored at this concentration, and diluted to an exact 0.005 normality as used. To prepare 0.100 *N* KIO_3, weigh exactly 3.567 g. into a 1-l. volumetric flask and dilute to the mark with water. To prepare approximately *N*/10 thiosulfate, dissolve 25 g. of $Na_2S_2O_3 \cdot 5\,H_2O$ plus 0.1 g. Na_2CO_3 in 1 l. of water. Allow the thiosulfate solution to stand a few days and then filter if necessary before standardizing. When the thiosulfate has been standardized, dilute the required amount of this solution along with 10 cc. of *N*/10 NaOH to 1 l. The required number of cc. of stock thiosulfate to give a liter of 0.005 *N* is obtained by dividing 5 by the normality of the stock thiosulfate.

To prepare the starch indicator solution, take 4 g. of indicator grade soluble starch, place with 10 mg. HgI_2 into a test tube, add a little water, and shake vigorously, then add slowly to 1 l. of boiling water. Continue boiling until solution is clear. Cool and transfer to a glass bottle.

The copper reduction value (CR value) is defined as the number of grams of copper reduced per 100 grams of fiber. Under the conditions described: Copper reduction value = 0.1272 (cc. thiosulfate for blank − cc. thiosulfate for sample).

Aqueous Extract pH Test

This test was carried out according to a procedure described in 1951 ([21], p. 567).

Alkali Centrifuge Value

Alkali centrifuge values were determined by a method described previously [22].

Arealometer Values

These values were determined on an arealometer, an instrument devised and described by Hertel and Craven [10]. Low-density plugs were used in all determinations except those shown in Figure 5, in

which high-density plugs were used of necessity because of the extreme range of values in the samples involved in this experiment.

Color Determinations

These measurements were carried out by Miss Dorothy Nickerson on a Nickerson-Hunter Colorimeter. The "increase in brownness" figures here reported are expressed in a simple arbitrary unit—the number of millimeters horizontal displacement of the color-index point on the chart used with this instrument.

Pressley Strength

The test was made on a conventional Pressley strength tester [2], using both "zero gap" and "1 mm. gap" jaws. Breaking strength figures and strength losses reported here are based on ten replicate breaks.

Length

Length determinations were carried out by the method listed in the 1944 Book of ASTM Standards ([3], p. 2019).

Susceptibility to Enzymatic Decomposition

The cellulase-containing filtrate used was prepared by growing the fungus *Myrothecium verrucaria* on raw cotton fiber in 500-cc. Erlenmeyer flasks in the presence of mineral salts, exactly as described for the preparation of "S factor" in an earlier paper [23]. Five cc. of this filtrate was placed into a 60-cc. bottle together with 10 mg. of raw cotton and the suspension shaken moderately on a laboratory shaker for 2 hr. at 20° C. The percentage of fiber fragmented was estimated by washing out the fragments from the fiber with a gentle stream of water and drying and weighing the remaining fiber.

X-Ray Angle

This property was determined as described by Berkley ([4], p. 57).

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The Reactivity of Keratin[1]

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Abstract

The amorphous phase of wool contains and is created by the amino acids with large sidechains. Among the latter are those which are commonly used in cross-linking reactions; since cross-linking is unlikely to have a profound effect on the elastic properties of a disorganized structure unless it occurs with very great frequency, it is now clear why cross-linking with agents such as formaldehyde fails to give desirable technical effects. A more promising method of modifying the properties of wool to commercial advantage is to form graft copolymers in the amorphous phase; possible methods of achieving this end are examined.

WHATEVER their defects, the synthetic fibers which have been developed during the past twenty years have set new standards of serviceability as regards such properties as tenacity, wear resistance, light resistance, and the dimensional stability which is associated with a low water adsorption. Although the best features of the various natural and manmade fibers are unlikely ever to be combined in any one fiber of the future, the consumer is clearly entitled to expect the manufacturer to provide a product which displays the combination of properties which is most appropriate to the end use. One method of meeting this requirement is, of course, to process blends of selected types of fiber; another is to modify the properties of one type of fiber by chemical means so that its inherent merits are supplemented in the desired way in a homogeneous fabric. Both methods are in common use, but this paper is concerned only with the second, and attention will be confined to wool.

The methods which have been evolved for modifying the properties of wool to practical advantage are of four main kinds. In order of decreasing commercial development these are (a) breakdown of cross-linkages (disulfide bonds) between the polypeptide chains, (b) formation of new cross-linkages between the polypeptide chains, (c) synthesis of polymers on or within the fibers, and (d) formation of cross-linkages between the reactive sidechains of keratin and those of the polymer synthesized within the fibers. Progress in all these fields of research, especially in the last three, has been handicapped by the almost complete absence of information about the order in which the amino acids are embodied in the polypeptide chains, about differences in composition between the crystalline and amorphous regions of keratin, and about the relative proportions of crystalline and amorphous material. However, it has been shown recently that there is an overwhelming preponderance of amorphous material in keratin [19], and the various lines of evidence which converge to provide a convincing proof of striking differences in composition between the crystalline and amorphous phases will now be summarized.

Differences in Composition between the Crystalline and Amorphous Phases of Wool Keratin

Progress in this study has been greatly facilitated by the work of Smith and his collaborators [9] on compositions of the crystalline and amorphous phases of natural silk. When a solution of silk, prepared by the technique of Coleman and Howitt [6], was subjected to the action of pancreatic enzymes at pH 7.8 and 40° C., a precipitate began to form after about 20 min., 55% of the original fibroin nitrogen being precipitated after about 24 hr. Amino acid analysis of the soluble and insoluble fractions, as well as of the unfractionated fibroin, gave the results shown in Table I. The insoluble fraction, which contains the highest proportion of the amino acids with short sidechains and the smallest proportion of bulky tyrosine sidechains, was shown by X-ray ex-

[1] A lecture given by Professor J. B. Speakman at the Joint Meeting of the Fiber Society and the Textile Institute in Boston, September 6, 1957.

amination to be highly crystalline and identical in structure with the crystalline regions of silk. Separation of the insoluble fraction is due mainly to the action of chymotrypsin in breaking the polypeptide chains at each tyrosine unit, thus giving fragments which, since they consist mainly of amino acids with short sidechains, can associate readily with one another. In the case of silk, therefore, the amorphous regions contain and are created by amino acid residues with bulky sidechains, while the crystalline regions consist of amino acid residues with small sidechains. In connection with later argument about the crystalline and amorphous phases of keratin, it is interesting to note that Smith and his collaborators [14] have been able to correlate the shapes of the load–extension diagrams of different varieties of silk with the proportions of amino acids with long side chains that they contain; the silks are placed in the same order—Tussah, Bombyx, Anaphe—as regards both ease of extension and content of amino acids with long sidechains.

In the light of these results, the crystalline and amorphous phases of keratin may be expected to consist preferentially of amino acids with short and long sidechains, respectively, and there is much evidence to support this view. Taking the amorphous phase first, it has been shown that the load–extension curves of human hair are coincident at extensions above 35% in water and 0.1 *N* hydrochloric acid, as shown in Figure 1 [22]. According to Astbury and Woods [1], the onset of the $\alpha \rightarrow \beta$ transformation, i.e., the extension of the crystalline phase of wool, is first perceptible at 20% extension, the transformation proceeding with increasing extension up to the breaking point, when little of the α-form is present. The salt linkage breakdown which is responsible for the weakening of animal fibers at extensions below 35% must, therefore, take place in the amorphous phase. In other words, the amino acid residues of lysine, arginine, aspartic acid, and glutamic acid are present in the amorphous phase but not in the crystalline phase. A further indication that the whole of the lysine in wool is present in the amorphous phase is to be found in the fact that complete reaction with 1-fluoro-2:4-dinitrobenzene is obtained in 48 hr. at 40° C. and pH 7.0 [18]. Similarly, since 96% of the tyrosine of wool can be converted into 3:5-di-iodotyrosine by treatment with a solution of iodine in ethanol for 72 hr. at 22.2° C. [20], the bulky tyrosine sidechains must be found mainly in the more readily accessible and presumably, therefore, amorphous regions of the fiber, just as in the case of silk.

There is thus much evidence to indicate that the amorphous regions of wool contain and are created by the amino acids with bulky sidechains, and the crystalline regions must, therefore, be rich in amino acids with short side chains. As yet, however, little precise information is available about the composition of the crystalline phase, though there appears to be some significance in the results obtained by Consden and Gordon [7] in their study of partial hydrolysates of wool. When wool is hydrolyzed with acids under mild conditions, it is to be expected that the more accessible amorphous regions of the fiber will be more vulnerable, and that the peptides present in partial hydrolysates will be derived prefer-

TABLE I. Mixed Enzyme Hydrolysis

Amino acid residue	Amount (g./100 g.) present in Fibroin	Soluble fraction	Insoluble fraction
Glycine	31.4	24.6	38.8
Alanine	26.3	21.6	31.2
Serine + threonine	16.3	11.8	20.8
Total	74.0	58.0	90.8
Tyrosine	10.3	19.1	2.3

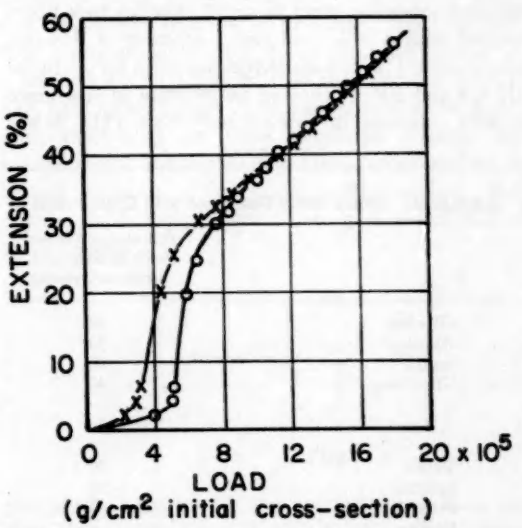


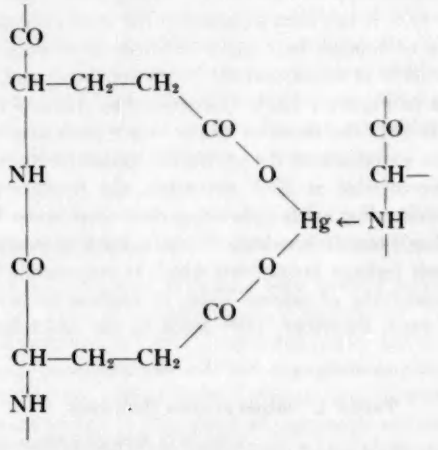
Fig. 1. Load vs. extension. O = fiber in water, X = fiber in 0.1 *N* HCL.

entially from the crystalline phase, though the effect of the amino acid environment on the reactivity of the peptide bonds cannot be ignored. Consden and Gordon hydrolyzed wool with 10 *N* hydrochloric acid for 10 days at 37° C., and, after separating the acidic peptides, treated the remainder with bromine and separated the fraction containing peptides of cysteic acid. In relation to the preceding argument, it is interesting that the amino acids with short sidechains, which constitute the crystalline phase of silk, should preponderate so heavily in the partial hydrolysate, as shown in Table II, especially as peptide bonds involving the amino group of serine are particularly labile.

But perhaps the main support for the theory comes from the fact that it serves to explain many puzzling features of the reactivity of keratin.

Cross-Linking Reactions

Since the basic and acidic sidechains of keratin are present in the amorphous phase, they must be readily accessible to cross-linking agents. Formaldehyde, which reacts with basic and amide side chains, was therefore expected to be capable of strengthening animal fibers, but treatment for 48 hr. with a 0.732% solution at the optimum pH of 6–7 gave only a 4.5% increase in the resistance of the human hair fibers to 30% extension in water [23]. Similarly, when the acidic sidechains are cross-linked with di-epoxides, the strengthening effect is small; human hair fibers treated with a 4% (vol./vol.) solution of 3:4-isopropylidene 1:2–5:6-dianhydromannitol for 24 hr. at pH 4.4 and 50° C. showed an increase in resistance to 30% extension in water of only 7.8% [5]. It has been customary to assume that the poor strengthening effect of formaldehyde is due to the inability of a small molecule to bridge the distance between the reactive sidechains, but no such explanation can be offered in the case of di-epoxides, for the molecules are larger. A much more reasonable explanation, now that the basic and acidic sidechains are known to be present in the amorphous phase, is that cross-linking is unlikely to have a profound effect on the elastic properties of a disorganized structure unless it occurs with very great frequency. How frequent the cross-linking must be is well indicated by the remarkable extent to which animal fibers may be strengthened by reaction with mercuric acetate; after being treated with a solution of mercuric acetate (0.1 *M*) in acetic acid (0.1 *N*) for 16 hr. at 22.2° C., the resistance of Lincoln wool fibers to 30% extension in water was increased by 36% [17]. The amount of mercury which combines with the keratin to produce this effect is at least 220 milli-equivalents/100 g. dry wool [4]. Since glutamylglutamic acid is the most abundant acidic dipeptide in partial hydrolysates of wool [8], and since mercury coordinates readily with nitrogen compounds, it seems probable that cross-linkages of the following type



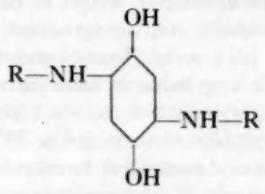
play an important part in reinforcing wool fibers to the extent which is necessary if valuable technical effects, such as unshrinkability, are to be obtained. Wherever and however the mercury combines with reactive sidechains, nitrogen atoms of neighboring main chains and their sidechains are always likely to be within easy reach, and it is on the ability to coordinate with nitrogen compounds that the effec-

TABLE II. Amino Acids Combined with Cysteic Acid

	Amount combined with cysteic acid (arbitrary units)
Glycine	34
Alanine	44
Serine	60
Threonine	40
Total	178
Valine	20
Leucine	18
Phenylalanine	4
Proline	–
Total	42

tiveness of mercuric acetate as a cross-linking agent really rests.

All the preceding observations, and especially the striking difference in effectiveness of formaldehyde and mercuric acetate as cross-linking agents, combine to show that very frequent cross-linking is essential for the reinforcement of the disorganized amorphous regions of keratin. At first sight, therefore, it is surprising that benzoquinone, which is believed to cross-link basic sidechains as follows



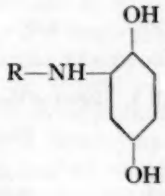
should be so much more effective than formaldehyde in reinforcing animal fibers; when human hair fibers were treated with a 1% solution in 5% (vol./vol.) alcohol for 48 hr. at 50° C. and pH 4.7, the increase in resistance to 30% extension in water was 20% [23]. In order to explain this result, it has been assumed that benzoquinone is able to cross-link more of the basic side-chains than formaldehyde because of the greater size of the molecule. This explanation has now been found to be untenable [10].

Doubt about the formation of covalent cross-linkages when wool is treated with benzoquinone was first aroused by the discovery that fibers which had been treated with a 1% solution of benzoquinone in 12.5% (vol./vol.) alcohol for 48 hr. at 50° C. and pH 4.96 contracted to 30% less than their original length as a result of extraction with the constant-boiling mixture of pyridine and water for 4 hr. in a Soxhlet apparatus. Untreated wool fibers did not supercontract under similar conditions, and the treated fibers should have been even more resistant if they are as heavily cross-linked as the increase in resistance to deformation suggests. If, however, benzoquinone reacts with basic sidechains without forming covalent cross-linkages, supercontraction is likely to be promoted, because deaminated fibers, for example, supercontract in boiling solutions of borax and sodium sulfite, whereas untreated fibers do not. Further studies of the supercontraction of benzoquinone-treated fibers were therefore undertaken.

After being treated with benzoquinone under the above conditions, approximately 5-cm. lengths of Lincoln wool fibers were mounted in stainless steel setting frames. By screwing the top clamp of each frame upwards, the fiber was drawn exactly taut and its precise length was measured by means of a traveling microscope. After the fiber had been slackened by screwing the top clamp downwards, the instrument was immersed for 1 hr. in a boiling solution of the appropriate reagent. At the end of this time the fiber was washed in three changes of distilled water, dried in complete absence of tension, and again drawn taut so that its length could be remeasured. Corresponding experiments were carried out with untreated fibers; values of the supercontraction given by (a) 2% borax, (b) 5% hydrated sodium sulfite, and (c) 5% sodium metabisulfite solutions are given in Table III, each value being the mean of 4–6 results. When a reagent forms stable covalent cross-linkages between the polypeptide chains of wool, supercontraction in a boiling solution of sodium bisulfite is prevented, and the fact that benzoquinone-treated fibers do supercontract to a marked extent suggests that they contain few, if any, new cross-linkages. Benzoquinone must, however, react with the basic sidechains, because the treated fibers, like deaminated fibers, supercontract in boiling solutions of borax and sodium sulfite. But reaction with basic sidechains to give sidechains of the following type

TABLE III. Supercontraction of Fibers

Reagent	Supercontraction of: Untreated fibers, %	Supercontraction of: Benzoquinone-treated fibers, %
Borax	−0.2	18.1
Sodium sulfite	0.7	31.1
Sodium metabisulfite	32.1	26.2



can hardly account for the marked increase in resistance to extension of benzoquinone-treated fibers. Part of the increase was found to be due to the

formation and deposition of a loose polymer of benzoquinone in the fibers during the 48-hr. treatment at 50° C.

A 2.5-g. pattern of all-wool flannel, which had been purified by extraction with alcohol and ether, followed by washing in distilled water, was treated with the solution of benzoquinone under the usual conditions, the liquor:wool ratio being 50:1. The pattern was then washed and dried; the gain in dry weight was 16.46%. It was found that the most suitable solvent for extracting polymer from the fibers is the constant boiling mixture of pyridine and water. The pattern was extracted with the mixture under three successive conditions of increasing severity, and the amounts of extract, dried over concentrated sulfuric acid and then over phosphorus pentoxide *in vacuo*, are given in Table IV, which includes corresponding values for untreated flannel. Extraction with the hot mixture causes severe degradation of the wool, as is indicated by the high value of the extract from the untreated flannel, but the bulk of the loose polymer can be removed from the treated flannel at 25° C. The effect of extraction for 4 hr. at 25° C. on the resistance of treated and untreated fibers to 30% extension in water at 22.2° C. is shown in Table V. It is clear, therefore, that about half [24.4 − (11.6 + 1.8) = 11.0] of the increased resistance to deformation of the benzoquinone-treated fibers is due to a loose deposit of polymer.

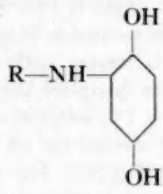
TABLE IV. Extraction of Flannel

Extraction conditions	Amount of extract (% on dry weight of untreated wool)	
	Untreated flannel	Treated flannel
100 ml., 4 hr. at 25° C.	0.18	5.65
100 ml., 2 hr. at 50° C.	0.09	1.75
Soxhlet, 4 hr.	5.08	2.50
Total	5.35	9.90

TABLE V. Effect of Extraction

Fibers	Change in resistance to extension, %	
	Before extraction	After extraction
Benzoquinone-treated	24.4	11.6
Untreated	—	−1.8

Extraction of polymer from the few fibers used in this experiment was undoubtedly more complete than with the flannel (Table IV), because the same volume of solvent was used in both cases, but it is in any case obvious that the whole of the increased resistance to deformation of benzoquinone-treated fibers cannot be referred solely to the internal deposit of polymer. Further, the balance of the increase cannot be referred to the combination of each basic sidechain with one molecule of benzoquinone. The maximum increase in weight to be expected on this basis is 8.64%, and in agreement with earlier observations [21] it has been found that reaction with the basic sidechains is incomplete. Since the observed gain in weight of the wool, after deducting the amounts of polymer extracted at 25° and 50° C., is 9.06%, it seems reasonable to conclude that more than one molecule of benzoquinone combines with each of the basic sidechains involved in the reaction. This conclusion is all the more reasonable because the weights of the extracts from the treated flannel (Table IV) are all too high, owing to the presence of combined pyridine as well as protein, as is shown by the fact that the fall in dry weight of the flannel was only 8.53% compared with 9.90% for the combined weights of the extracts. It seems probable, therefore, that after



sidechains have been formed by reaction with one molecule of benzoquinone, the new sidechains take part in polymerization with more quinone, thus forming a graft copolymer of protein and quinone. The graft copolymer, through hydrogen bonding as well as steric hindrance, will cause a profound alteration in the elastic properties of the fibers and is regarded as being the second factor responsible for the increased resistance to deformation of benzoquinone-treated fibers in water.

Polymerization Reactions

Three methods of synthesizing polymers inside wool fibers have so far been developed in these laboratories. They involve (a) treatment with the

vapors of water and monomer [3], (b) applying a solution containing hydrogen peroxide and monomer to wool containing ferrous ions [13], and (c) treatment with a solution containing potassium persulfate and monomer [15]. In the case of polymethacrylamide, subsequent treatment with formaldehyde leads to the formation of a graft copolymer [13], but in the absence of some such reaction the bulk of the polymer seems to be a loose deposit. Because the deposit is loose, the increased resistance to deformation of the treated fibers does not survive repeated extension, as in the case of polyethylene sulfide [3]. In the light of the preceding work on the action of benzoquinone on wool, it seems probable that more effective alteration of the elastic properties of the fibers could be obtained with smaller amounts of polymer, if the latter is anchored to the fiber as a graft copolymer. Three lines of attack on this problem are being pursued.

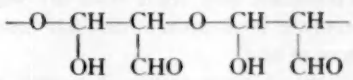
Oxidation polymerization. In this case, it was hoped that anchoring of the polymer would be realized through the free radicals formed in the course of polymerization. The reaction chosen for examination was the formation of pigments by oxidizing *p*-phenylene diamine with hydrogen peroxide.

Six Lincoln wool fibers, which had been calibrated by determining their load–extension curves up to 30% in distilled water at 22.2° C., were attached to a 2.5-g. pattern of purified flannel and steeped for 24 hr. at 25° C. in 125 ml. of a solution containing hydrated copper sulfate (0.4%) and acetic acid (0.2%). After the pattern had been rinsed in three changes of distilled water, it was immersed in 125 ml. of a pH 8 buffer solution containing *p*-phenylene diamine (1.25 g.) for 10 min. before adding 17 ml. of 3.4% (wt./vol.) hydrogen peroxide. The reaction was allowed to proceed for 24 hr. at 25° C.; the pattern was then removed and washed in running water overnight before the fibers were separated for restretching. The average increase in resistance to extension of the fibers was 18.1%; the gain in dry weight of the pattern was 12.30%. When the pattern was extracted with the constant boiling mixture of pyridine and water, much of the pigment was easily removed, as is shown by the data of Table VI. After the series of extractions, the treated pattern was still highly colored, and the fact that the total amount extracted (13.32%) exceeds the original gain in weight (12.30%) is, of course, due to loss of protein. Since, however, so much of the pigment is easily extracted, and since the remainder seems to be incapable of giving any notable protection of the protein against dissolution by the hot constant boiling mixture (compare Table IV and Table VI), it seems clear that the action of the pigment in increasing the resistance of the fibers to extension is due mainly to the steric effects of a loose deposit of polymer. Part of the pigment may be present as a graft copolymer, but the amount cannot exceed 12.30 − 8.30 = 4.00%, and is likely to be much smaller. Attention was, therefore, turned to other possible means of forming graft copolymers.

TABLE VI. Extraction of Flannel

Extraction conditions	Amount of extract (% on dry weight of untreated wool)	
	Untreated flannel	Treated flannel
100 ml., 4 hr. at 25° C.	0.18	6.79
100 ml., 2 hr. at 50° C.	0.09	1.51
Soxhlet, 4 hr.	5.08	5.02
Total	5.35	13.32

The action of reductone [26] *on keratin* [11]. The principle underlying these experiments is that of using a polymerizable compound which is capable also of forming covalent bonds with keratin. Reductone was chosen because it should be capable of combining with basic sidechains, and it polymerizes with great ease to give a polymer which is believed, on the basis of evidence that will be reported elsewhere, to have the following constitution:



When human hair fibers were treated with a mixture of reductone (0.5 g.) and water (5 ml.) for 48 hr. at 25° C., the increase in the resistance of the fibers to 25% extension in water was 54.0%. A 0.1-g. sample of Lincoln wool, treated with the same amount of the aqueous solution of reductone under the same conditions, showed an increase in dry weight of 60.3%. It seems probable that the polymer formed at 25° C. is loosely deposited within the fibers, because the marked strengthening does not survive the first extension of the treated fiber. When, however, the reaction is carried out at 50° C., the strengthening survives repeated extension and the polymer, unlike that formed at 25° C., is almost

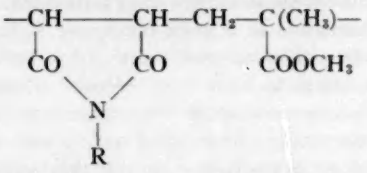
completely resistant to extraction by 0.1 *N* hydrochloric acid. Since von Euler et al. [25] have shown that reductone reacts with *p*-nitroaniline to give the following compound

$$NO_2—C_6H_4—NH—CH=C(OH)—CHO$$

and since treatment with reductone causes no change in weight or resistance to extension with deaminated wool and hair, it seems safe to conclude that a graft copolymer is formed when wool reacts with reductone at 50° C., the structure being reinforced by combination of the aldehyde groups of the polymer with reactive sidechains of the polypeptide chains as well as by hydrogen bonding and steric hindrance.

Copolymers with combined maleic anhydride [24]. The third attempt to form graft copolymers arose from the discovery that wool can be protected against heat degradation by introducing unsaturated compounds into the fibers [16]. When, for example, an all-wool flannel was treated with maleic anhydride, which combines with the basic sidechains of keratin, subsequent heating in an atmosphere of dry nitrogen for 24 hr. at 150° C. gave a fabric which was much more resistant to dissolution in sodium hydroxide and urea-bisulfite solutions than the heated untreated flannel. Data for samples of flannel containing different amounts of maleic anhydride are given in Table VII, which includes corresponding data for one sample containing succinic anhydride. Comparison of the results for maleic and succinic anhydride suggests that the protective effect of the former is due to the formation of addition compounds (therefore, new cross-linkages) with thiols derived from the breakdown of disulfide bonds under the influence of heat.

In the light of these results it seemed probable that graft copolymers might be formed very easily by applying vinyl compounds to wool previously treated with maleic anhydride. Preferential internal polymerization of the monomer may be brought about in several ways [3, 13, 15], and a graft copolymer of the following type is obtained



By varying the nature of the monomer a wide variety of properties can, of course, be conferred on the reinforced fibers.

The importance of graft copolymerization is not, however, confined to reactions which take place preferentially in the amorphous phase. It has already been shown [2] that one of the most promising methods of modifying the properties of wool is by forming an anchored film of polymer on the surface of the fibers; with anhydrocarboxyglycine, dimensional stability, unshrinkability, and greatly increased resistance to wear were obtained with no more than 3% by weight of polymer. Despite its advantages, little use has so far been made of the method because anhydrocarboxyglycine is not available in commercial quantities. Fortunately, other methods of achieving the same end are now available. If, for example, flannel is impregnated with a solution of maleic anhydride in an inert organic solvent and then heated for 30 min. or longer at 85° C., subsequent impregnation with a solution of methyl methacrylate and benzoyl peroxide (0.5% on the weight of monomer) in an inert organic solvent followed by heating at the same temperature leads to the formation of an anchored film of copolymer on the surface of the fibers. Alternatively, as has been proposed by Kropa and Nyquist [12], a solution of the preformed copolymer may be applied to the fabric, followed by baking.

In conclusion, therefore, the general argument of this paper may be summarized as follows: the wool fiber contains such a high proportion of disorganized, amorphous material that simple cross-linking reactions are unable to modify the properties of wool to an extent which is commercially useful unless the reagent is polyfunctional and capable of reaction with groups which occur with great frequency in the fiber. One such reagent is mercuric acetate, which owes its success to the ease with which

TABLE VII. Flannel Containing Maleic Anhydride

Combined maleic anhydride (m. moles/g. dry wool)	Alkali solubility, %	Urea-bisulfite solubility, %
—	13.3	13.9
0.08	8.1	6.9
0.17	6.8	1.3
0.45	4.6	− 2.5
0.65	2.6	− 4.9
0.86	0.7	− 7.9
1.12	−1.1	−11.2
1.10 (succinic anhydride)	81.5	32.2

mercury salts coordinate with nitrogen-containing compounds. A much more promising method of producing chemically modified wools is by processes which lead to the formation of graft copolymers inside or outside the fibers; a new general method of achieving this end has been outlined.

Acknowledgment

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Improved Light and Weather Resistance of Cotton Resulting from Mercerization

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Abstract

Comparative exposures of mercerized and unmercerized cotton to light and to weathering brought out anomalous effects in the breakdown of cotton cellulose. There was less deterioration of the mercerized cotton, as measured by the ability of the fabric to resist rupture by tension (measured by breaking strength), but at the same time, more degradation (as determined by fluidity measurements), indicating a reduction in average degree of polymerization of the cellulose.

These observations are consistent with reports in the literature that mercerized cotton is somewhat more susceptible to oxidation and to hydrolysis than comparable unmercerized cotton. The behavior in exposure to light evidently is part of a general phenomenon, because higher fluidities have been observed for the chemically reactive mercerized cottons under conditions where the strength losses for mercerized and unmercerized cottons were equal.

The higher retention of strength by the mercerized cotton may represent a significant advantage, because it promises a longer service life of mercerized goods when deterioration occurs mainly from exposure to sunlight. When ordinary unmercerized cotton has lost half strength, corresponding mercerized cotton can be expected to last for ¼ to ½ longer before reaching that level.

MERCERIZED cotton has been found to withstand degradation better than unmercerized cotton when exposed to weather. The difference may amount to ¼ to ½ longer service life for the mercerized fabric. This investigation demonstrates the improved resistance of mercerized cotton to sunlight and weathering over unmercerized cotton and suggests an improved base fabric for further finishing. The tests described in this report were intended to represent practical conditions of ordinary cotton finishing.

Somewhat similar improved resistance of mercerized over unmercerized cotton to heat [4, 5] and to oxidation and hydrolysis by chemical agents [10, 11, 12] has already been shown.

Since mercerization of cloth is a relatively inexpensive process, it offers a means of extending the life of cotton products in end uses where better resistance to the deteriorating influences of weathering, especially strong sunlight, is required.

Our observations of improved resistance to sunlight confirm reports in the literature, if change in breaking strength is regarded as the measure of breakdown by light. The result is anomalous, however, if the fluidity values in cuprammonium hydroxide or cupriethylene diamine hydroxide are accepted as a measure of the breakdown. The observed fluidity values for mercerized samples after weather exposure were higher than the values obtained for unmercerized cotton. Similar anomalous results have been reported for oxidation and hydrolysis of comparable mercerized and unmercerized materials, but no previous record has been found of the effect of light on both strength and fluidity (or viscosity) of mercerized as well as unmercerized cotton.

Background Information

Some confusion exists in the literature because of the erroneous assumption that breaking strength results and fluidity values measure the same property, and that this property may be described interchangeably as degradation, deterioration, or breakdown,

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etc. For clearness, let us use the term deterioration to refer to reduction in desirable "in use" properties and degradation to describe a change of a chemical nature in molecular structure.

Breaking strength measures the ability of a fabric to resist rupture by means of tension, whereas fluidity is a measure of the breakdown of chain length, since it measures the reduction in average degree of polymerization. If the cellulose chain breaks close to the end, the reduction in average degree of polymerization is not great. If the chains break in the center of the molecule, this affects the average a great deal more. With this in mind, it is clear that the loss in breaking strength may be high, whereas the change in fluidity measurements may or may not be large. Thus it is obvious that the two tests do not measure the same quantity.

In the literature, practically nothing supported by specific observations has been found on the comparative resistance of mercerized and unmercerized cotton to solar radiation; there is information on comparable fluidities and susceptibility to chemical action of mercerized and unmercerized cotton.

After some earlier disagreement in reports, it was shown clearly [12] that mercerization alone should not cause any change in fluidity of cotton cellulose, and it is now generally accepted that mercerization does not bring about deterioration.

It is also generally recognized that mercerized cotton is more susceptible to chemical reaction than unmercerized, and, in accordance with this property, mercerized cotton tends to oxidize and hydrolyze more readily than unmercerized and degrades more easily. These effects are shown by higher fluidities of the mercerized material. Ridge and Bowden [11] have shown curves for the strengths of mercerized and unmercerized cotton oxidized by hypochlorite plotted against cuprammonium fluidities. Within the range of fluidities from 4 to 35 rhes and of strength retained down to about 50% oxidized (approximately the ranges under discussion in this paper), mercerized cottons retained higher strength and showed higher fluidities than comparable oxidized unmercerized cottons. To sum up, the mercerized shows less deterioration (measured by breaking strength) than the unmercerized, but more degradation (measured by fluidity) than the unmercerized.

A somewhat greater stability of mercerized cotton over comparable unmercerized material to heat has been reported [4, 5]. In these studies, exceptions were found to this behavior, and the conditions necessary for such heat resistance have not been fully established. Possible improvement in this property of mercerized cotton was not followed further because, at the time it was noted, the heat resistance of partially acetylated cotton had been found to be much greater.

It has been stated that mercerized cotton withstands exposure to radiation from ultraviolet lamps or sunlight better than unmercerized cotton. Heermann and Sommer [6] reported, on the basis of a few exposures which were not strictly comparable, that mercerized cotton yarns lost less strength than unmercerized under ultraviolet light. Kleinert and Moessmer [9] recently noted that in practical experience lustrous cotton (such as Egyptian) and mercerized cotton are less damaged by light than cotton low in luster. This is similar to statements noted in earlier publications (for example, that by Henk [7], possibly from the same source not yet identified); no evidence for such statements has yet been found.

Appreciable amounts of free alkali or acid can be expected to increase the degradation of cellulose in sunlight; for example, small but measurable amounts of sulfuric acid in rayon accelerate degradation [9]. Also, an unauthenticated statement is recalled to the effect that cotton "finished on the acid side" will be less resistant to light than cotton "finished on the alkaline side."

The conclusion would be drawn from the evidence given above (and has, in fact, been stated [10]) that mercerized cotton behaves differently from unmercerized and that the fluidity–strength relationship is different.

Materials and Methods

The materials were prepared with the original purpose of making a simple practical test to determine differences in the effect of exposure to light, with and without other factors of weathering. Half of a piece of bleached 80 × 80 print cloth was mercerized in the ordinary manner (with tension) in a finishing plant; these original bleached unmercerized and mercerized materials were taken as the base fabrics. Portions of them were exposed to weathering and to sunlight at different seasons of the year as described below, without any further treatment.

In addition, for the three earlier sets, a portion of each base fabric was immersed in a 1% solution of

sulfuric acid for 1 min. and thoroughly washed with distilled water. Another portion of each was immersed in a 1% solution of sodium carbonate and well washed.

The purpose of the latter two treatments was to show whether finishing through acid or alkali would cause any notable differences in the results. There was no intention of determining the effects of any specific quantities of acid or alkali. The alkali-treated samples gave assurance that at least one set of samples was free from acid; and the final results indicated no undue effect from either acid or alkali in any of these samples.

Exposures of samples representing all of the different treatments were made in New Orleans on weathering racks set at a 45° angle, facing south; similar samples were exposed under glass under the same conditions for the same periods of time. Two experiments, designated *A* and *B*, were run. Experiment *A* was started in October 1953, and *B* in November 1955; the same fabric was used in both experiments. The primary purpose of Experiment *B* was to check and extend the results of Experiment *A*. In *A* the exposure periods were of six months each (Set I, October 2, 1953–April 1, 1954; Set II, February 11, 1954–August 10, 1954; and Set III, July 18, 1954–January 17, 1955). The three exposures of duplicate samples started at different times and covered a total period of more than a calendar year. There was overlapping and more exposure hours from fall to spring than during the hottest summer months, so the weathering was not the most severe that would have been possible. Samples for two of the comparisons were lacking in the second set, which was exposed under the most severe of the weathering conditions.

Experiment *B*, consisting of six sets of eight samples, each set containing four mercerized and four unmercerized samples, were weathered both in the open and under glass. Three of the six sets of samples were weathered for a period of 6 mo. and three sets were weathered for 12 mo. Since the results of Experiment *A* did not show substantial differences for fabrics finished on the acid or alkaline side, these pretreatments were omitted in Experiment *B*. In Experiment *B* the six sets, designated IV through IX, were placed on the racks at staggered intervals; in this way each set was exposed at some time to the extremely hot summer weather, as well as to the milder seasons. Set IV was placed on the

TABLE I. Breaking Strength and Fluidity Values of Unweathered Fabrics*

	Unmercerized		Mercerized	
	Breaking strength†, lbs.	Fluidity	Breaking strength‡, lbs.	Fluidity
Base fabric	59.8	4.82	54.8	5.32
Alkali-treated	60.1	4.70	57.2	5.45
Acid-treated	57.4	5.56	54.9	6.98

* ASTM Method A, Dispersions in Cuprammonium Hydroxide.
† 92 threads/in.
‡ 89 threads/in.

TABLE II. Percentage of Strength Retained After Six Months Weathering in Experiment *A*

	Unmercerized						Mercerized					
	Under glass			Open exposure			Under glass			Open exposure		
	Base fabric	Alk.	Acid	Base fabric	Alk.	Acid	Base fabric	Alk.	Acid	Base fabric	Alk.	Acid
Set I Oct.–Apr.	74	72	71	71	69	73	89	83	76	86	82	76
Set II Feb.–Aug.	—	69	66	50	52	—	—	67	78	74	67	—
Set III July–Jan.	79	70	76	67	69	67	89	80	78	79	75	72
Averages of Sets I and III only	76.5	71	73.5	69	69	70	89	81.5	77	82.5	78.5	74
Averages of 8 from each group			72			65			80			76
Grand average of 16 values						68.5						78.2

Strengths of unexposed base fabrics are shown in Table I.

racks November 1, 1955; Set V, December 1, 1955; Set VI, February 1, 1956; Set VII, March 1, 1956; Set VIII, April 9, 1956; and Set IX, May 11, 1956.

Mildew is frequently a factor in weathering, but there was practically no visual evidence of mildew on the exposed samples; any suspicious areas were avoided in cutting samples for testing. The breaking strength tests were made by the strip method in the warp direction, on samples with the same numbers of threads as in 1-inch widths of the original bleached or bleached and mercerized goods. For convenience, results from exposures are shown as percentages retained, based on these strengths.

The fluidities were determined by two ASTM methods [1]. Sets I through III were determined substantially by ASTM Method A (Dispersions in Cuprammonium Hydroxide), with slight modifications in accordance with Conrad and Tripp [2]. Sets IV through IX were determined by ASTM Method B (Dispersions in Cupriethylene Diamine Hydroxide). In the first three sets the cuprammonium fluidity of the mercerized base fabric was only half a unit higher than that of the unmercerized. The changes in fluidity from alkali treatment were too small to be significant. After the acid treatment, fluidities were about ¾ to 1½ units higher than before treatment, for the unmercerized and mercerized samples, respectively.

Discussion of Results

The results are shown in terms of breaking strengths retained after exposure in Tables II, IV, and V and in terms of fluidities in Tables III and VI. Values are shown only for tests made on samples exposed for either 6 or 12 mo., although other samples were tested at intermediate periods. There are a few "out" values, not accounted for in experiment.

Breaking Strength

The values for breaking strength as a measure of deterioration fall into a consistent overall pattern. Since they are based on sunlight and weathering tests, which are by no means definite, averages are more significant than individual values.

Because of missing values in the second set of Experiment *A*, averages are shown first in Table II for Sets I and III only, which were exposed mostly in the fall and winter months. Deterioration of unmercerized material may be slightly greater after either alkali or acid treatment than in the case of untreated, and slightly greater in open exposure than under glass. Quantitative statements are hardly justified by the date. Deterioration of mercerized material is greater for both the alkali and the acid treated samples, and greater under full exposure than under glass.

For a better comparison of open exposure with that under glass, the groups of eight values for each type of cotton, mercerized and unmercerized, under each condition, were averaged together in Table II. As would probably be expected, there was less deterioration under glass than open to the weather, and distinctly less deterioration of the mercerized than of the unmercerized fabrics.

TABLE III. Fluidity Values After Six Months Weathering in Experiment *A*

	Unmercerized						Mercerized					
	Under glass			Open exposure			Under glass			Open exposure		
	Base fabric	Alk.	Acid	Base fabric	Alk.	Acid	Base fabric	Alk.	Acid	Base fabric	Alk.	Acid
Set I Oct.–Apr.	20.8	21.4	21.5	20.1	20.0	20.6	24.8	21.4	24.5	25.8	26.1	25.8
Set II Feb.–Aug.	18.5	17.1	18.4	22.9	23.6	21.2	—	30.3	26.0	27.1	26.3	—
Set III July–Jan.	19.5	19.6	21.1	21.4	22.0	22.4	23.0	28.7	31.1	25.5	26.3	30.4
Averages of Sets I and III only	20.2	20.5	21.3	20.8	21.0	21.5	23.9	21.4	24.5	25.7	26.3	28.1
Averages of 8 from each group			19.9			21.6			24.5			26.7
Grand average of 16 values			20.8									25.4

Fluidities for unexposed base fabrics are shown in Table I.

TABLE IV. Percentage of Strength Retained After Six Months Weathering in Experiment *B*

	Unmercerized		Mercerized	
	Under glass	Open exposure	Under glass	Open exposure
Set IV	74	65	87	78
Set V	67	62	84	75
Set VI	70	57	81	70
Set VII	70	56	77	70
Set VIII	70	60	84	80
Set IX	77	66	89	81
Average	71.3	61.0	83.6	78.3
Grand average	66.1		81.0	

Note: Each number represents an average of ten breaks from two different samples of fabric taken from different parts of the roll and weathered in different places on the rack.

Finally, the averages were taken for all 16 of the unmercerized and for the 16 mercerized samples for the principal comparison. These results showed 78.2% retention of strength by the mercerized samples and 68.5% by the unmercerized, these overall values being significantly different. Although the differences between the retention of strength of corresponding mercerized and unmercerized samples were not all of similar magnitude, the mercerized material was relatively stronger in every case but one.

The numerical difference between the overall values, each an average of 80 breaking tests on fabrics which were supposed to be substantially the same initially, was 9.7%, which corresponds with a relative difference of 14% based on the unmercerized material.

It can be predicted from Table II that at the end of a reasonable service life of the unmercerized cloth, taken as the time required for deterioration to 50% strength, the mercerized would last from $\frac{1}{4}$ to $\frac{1}{3}$ longer in situations where the deterioration was due mainly to the effects of sunlight. This prediction is based on a pattern of weathering established by Dean and Worner [3]. Their curve for strength losses, translated into retentions for different cottons upon weathering, diverged for three months and then continued approximately parallel, but all at a decreasing slope, to the end of the year. According to these curves, numerical difference observed at 6 mo. should continue, and would work out to $\frac{1}{4}$ to $\frac{1}{3}$ longer life of the mercerized material until it too lost 50% of its strength.

The results of Experiment *B* are very similar to those of *A*. Breaking strength results for all six sets of samples for 6 mo. are shown in Table IV and for three sets of samples for 12 mo. in Table V. Each figure in these tables represents an average of ten breaks from two samples in different locations on the racks. The breaking strength results follow the same pattern as in Table II. Averages of the six sets in Table IV show 81.0% retention for the mercerized samples and 66.1% for the unmercerized after 6 mo. weathering. These values are in good agreement with the corresponding 78.2% and 68.5% obtained in Experiment *A*. Here, however, the mercerized is about 22% stronger than the unmercerized. After 12 mo. the values are 61% for the mercerized and 45% for the unmercerized, as shown in Table V. This falls in line very well with the predictions made after the 6 mo. weathering of Experiment *A*. After 12 mo., the mercerized samples retained 35% greater strength than the unmercerized.

Fluidity Determinations

A most striking result is that the fluidities of the exposed mercerized samples were higher than those of the corresponding unmercerized samples. In the only exceptional case the values were equal.

This overall result is notable because the greater strength retained by the mercerized cloth implies that it is in better condition after exposure than the unmercerized, but the higher fluidity indicates a higher degree of degradation. Thus, the mercerized fabric has undergone greater chemical change in molecular structure. There has been breakdown in the length of the cellulose chains, resulting in a reduction in average degree of polymerization. Hence, fluidity determinations did not serve to confirm the greater durability of the mercerized fabric which was indicated by its strength.

Averages of fluidity values in Tables III and VI indicate that full exposure to weathering was slightly more severe on both mercerized and unmercerized cottons than than exposure under glass. The acid and alkali treated unmercerized samples used in the first three sets show no consistently higher fluidity (or greater degradation) than the untreated. The acid and alkali treated mercerized fabrics tended to have higher fluidities (although results are somewhat erratic) and greater degradations, as indicated also by the differences in strengths reported above. In

Table III the grand average of values of fluidities of the 16 unmercerized samples was 20.8 rhes and that of the 16 mercerized samples was 25.4. In Table VI, obtained from Experiment *B*, the average value for mercerized was 22.7 rhes as compared to 19.4 for unmercerized. In other words, there was significant evidence of more structural degradation of the mercerized cotton, even though there was definitely greater retention of strength.

Explanation of Results

A simple and superficially plausible explanation for the significantly greater resistance of the mercerized cotton to light was based on greater reflection of the incident light, leaving less to be absorbed and to promote chemical action on the cellulose. This is the explanation given by Kleinert and Moessmer [9], but no evidence was presented. Such an explanation seems to be unacceptable on at least two counts. First, in spite of its luster, mercerized cotton does not reflect more of the total incident light than unmercerized. This was reported by Jacoby [8] from spectrophotometric measurements on samples of mercerized and unmercerized materials from the same original piece of bleached goods. Second, any such difference in reflection would not account for the greater degradation according to fluidity.

No specific explanation has been found for the different behavior of mercerized from unmercerized cotton upon exposure to sunlight, or to other types of oxidation and hydrolysis, nor for their anomalous features. All of these reactions presumably depend upon the greater proportion of chain molecules made more accessible to reaction by mercerization. Oxidation in sunlight, for example, would be expected to proceed farther and more readily in accordance with the recognized greater reactivity of mercerized cotton, and it does, insofar as chemical breakdown or reduction in average degree of polymerization is indicated by the observed fluidities. The effect of mercerization unquestionably includes some form of rearrangement within the cotton fiber. If more cellulose chains are shortened in the mercerized coton than in the unmercerized, perhaps some of these chains are no longer essential to strength. There may be other factors in the explanation; possible effects of alkali sensitivity when dissolving in cuprammonium solution should not be overlooked.

Summary

Ordinary commercially mercerized bleached cotton cloth was found to resist deterioration upon exposure under glass to sunlight, or to the full effects of weathering in the New Orleans climate, better than the same cloth not mercerized. This was shown by about 14% better retention of strength at the end of 6 mo. exposure in one experiment and by about 22% in a second experiment. At the end of 12 mo. exposure mercerized fabric retained about 35% more strength than unmercerized material. On the other hand, in fluidity tests by both the cuprammonium hydroxide and cupriethylene diamine hydroxide methods on the same exposed materials, higher fluidities for the mercerized exposed samples indicated greater degradation (cellulose chain breakdown) for the mercerized cotton.

This behavior is consistent with reports in the literature from which one can conclude that mercerized cotton will withstand oxidation and hydroly-

TABLE V. Percentage Breaking Strength Retained After Twelve Months Weathering

(Six sets, eight samples each, weathered for a total of twelve months, November 1955 to May 11, 1957)

	Unmercerized		Mercerized	
	Under glass	Open exposure	Under glass	Open exposure
Set VI	56	—	70	—
Set VII	52	36	66	49
Set VIII	51	37	71	55
Averages	53	37	69	52
Grand average	45		61	

TABLE VI. Fluidity Values After Six Months Weathering

	Unmercerized		Mercerized	
	Under glass	Open exposure	Under glass	Open exposure
Set IV	19.3	17.9	23.3	22.6
Set V	19.7	17.9	20.0	22.4
Set VI	19.1	22.5	22.4	25.5
Averages	19.4	19.4	21.9	23.5
Grand average	19.4		22.7	

ASTM Method B, Dispersions in Cupriethylene Diamine Hydroxide.

sis with less loss of strength than unmercerized cotton, but here also it showed higher fluidities after such treatments than unmercerized cotton.

Mercerized cotton is sufficiently superior in strength retention to suggest that advantage could be taken of it to obtain cotton end products of longer service life where deterioration is due mainly to the effects of sunlight. Its greater retention of strength under chemical attack supports this view. Whether the strength retention is sufficient of itself to allow appreciably longer life under conditions of oxidative or hydrolytic attack apparently has had little attention. Mercerized cotton could be tried for use under such conditions with very little expense or trouble.

Acknowledgments

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Concerning the Theory of Fatigue Failure in Textile Materials

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Abstract

A minor modification of the reaction rate theory of flow is proposed with the aim of accounting, in terms of molecular processes, for the observed dependence of dynamic properties, particularly fatigue, on the frequency of stressing. To this end a factor $\phi(\nu)$, which is a function of the frequency ν, is introduced into the expression for the rate of breakage of bonds in the macromolecules of textile materials. It is shown that with this reasonable assumption of a frequency factor there results a general expression which, like earlier expressions, is compatible with the known dependence of fatigue life on temperature and stress under dynamic as well as dead loads. The present development goes further, permitting the derivation of a specific expression which is in accord with the observed frequency dependence of the fatigue life of a textile material.

Introduction

The fatigue performance of textiles and other polymeric materials under various technologically significant conditions has been well explored in the empirical manner. A comprehensive and critical review of the field has been given by Dillon [5]. In comparison with the amount and kinds of study which have been devoted to the other aspects of mechanical behavior, however, the investigation of the basic processes involved in fatigue and their interpretation at the atomic or molecular level have been rather neglected. In particular, little attention has been given to theoretical treatment of the influence of periodicity of stressing, an important feature of fatigue as well as of other mechanical phenomena. The present paper proposes a modification of Eyring's statistico-mechanical rate theory of flow [6], introducing the concept of the dependence of molecular processes on the frequency of stressing.

Theoretical Considerations

It can readily be shown, following the line of reasoning employed by Tobolsky and Eyring [9], that for the application of a steady stress f to a condensed molecular structure, with a symmetrical potential-energy barrier, the reaction rate theory gives for the net frequency of forward jumps

$$r_n = r\left[\exp\left(f\lambda/2NkT\right) - \exp\left(-f\lambda/2NkT\right)\right] \quad (1)$$

where $r = \frac{kT}{h}\exp\left(-F^*/RT\right)$, k = Boltzmann's constant, h = Planck's constant, T = absolute temperature, F^* = free energy of activation per mole for the rupture process, R = universal gas constant, λ = distance between equilibrium positions before and after rupture, and N = number of bonds per unit cross section at any instant. Evidently f/N represents the average force applied to each bond.

The foregoing Equation 1 arises from probability considerations, namely the probability that the particle involved in the flow or deformation will have sufficient energy to surmount a potential barrier. We now introduce the assumption that with each periodic application of stress the probability of bond breakage is increased above the level prevailing in the simple constant-load case. This concept is partially based on the assumption of inertial effects, operative in each oscillation, for which adequate provision may not be made by the theory as developed for the steady-load case. It is reasonable to assume that the frequency of bond breakage, on account of the periodic-stress factor, will be dependent on the number of times in unit time ν that the maximum stress is attained.

Let the frequency of bond breakage then be proportional to the product $\phi(\nu)r_n$, where $\phi(\nu)$ is a monotonically increasing function of ν, of such form that $\phi(0) \neq 0$. It will be seen that the latter

restriction is necessary in order that the product $\phi(\nu)r_n$ not vanish for the case of a static load ($\nu = 0$). Under dynamic conditions the quantity f in Equation 1 is to be taken as a constant, representative stress—for example, the average stress or the stress-amplitude.

If now it is assumed that f is sufficiently large to effect permanent bond breakage (i.e., without the reformation of equivalent bonds) in substantially all the transfer processes, each of these processes represents the disappearance of an intact bond. Then, since the rate of transfer r_n refers to unit concentration of particles or bonds involved in the rupture process, the rate of decrease in the number of bonds N will be

$$-\frac{dN}{dt} = \phi(\nu)r_nN \tag{2}$$

$\phi(\nu)$ evidently can be so defined as to include the required proportionality factor without violating the condition $\phi(0) \neq 0$.

For sufficiently large f, furthermore, the term $\exp(-f\lambda/2NkT)$ in Equation 1, representing the probability of a backward jump, becomes negligible and can be omitted.[1] Then we have

$$-\frac{1}{N}\frac{dN}{dt} = \phi(\nu)\frac{kT}{h} \exp(-F^*/RT)\exp(f\lambda/2NkT) \tag{3}$$

To integrate this equation according to the procedure employed by Tobolsky and Eyring for their corresponding equation, let $x = f\lambda/2NkT$. On substituting and rearranging, we can write

$$\int \frac{\exp(-x)}{x}\,dx = \phi(\nu)\frac{kT}{h} \times \exp(-F^*/RT)\int dt \tag{4}$$

The limits of integration are given by the following considerations. $N = N_0$, the initial number of bonds/cm.[2] when time $t = 0$.[2] Rupture occurs when f/N is indefinitely large ($f/N \to \infty$). It follows that $N = 0$ at $t = L$, the "fatigue" lifetime of the sample. Then $x = x_0 = f\lambda/2N_0kT$ when $N = N_0$ and $t = 0$, and $x = \infty$ when $N = 0$ and $t = L$. Hence, we have

$$\int_{f\lambda/2N_0kT}^{\infty} \frac{\exp(-x)}{x}\,dx = \phi(\nu)\frac{kT}{h} \times \exp(-F^*/RT)\int_0^L dt \tag{5}$$

Examination of a table of numerical values [7] of the integral

$$\int_{x_0}^{\infty} \frac{\exp(-x)}{x}\,dx \equiv -Ei(-x_0)$$

indicates that for large values of x_0 ($x_0 > 10$),

$$-Ei(-x_0) \cong \frac{\exp(-x_0)}{x_0}$$

Hence we may write Equation 5

$$\frac{\exp(-f\lambda/2N_0kT)}{f\lambda/2N_0kT} = \phi(\nu)\frac{kT}{h}\exp(-F^*/RT)\,L$$

or

$$\ln L = -\frac{f\lambda}{2N_0kT} - \ln\frac{f\lambda}{2N_0h} - \ln\phi(\nu) + \frac{F^*}{RT} \tag{6}$$

[1] For nylon 66, for instance, it appears from estimates assuming perfectly parallel, efficiently packed molecular chains that $f\lambda/N$ is of the order of 10^{-12} ergs/bond for stresses ranging from those causing appreciable flow to those causing rupture. Hence, at about room temperature ($T = 300°$ K.),

$$\frac{f\lambda}{2NkT} = \frac{10^{-12}}{2 \times 1.38 \times 10^{-16} \times 3 \times 10^2} = 12$$

and

$$\exp\left(\frac{f\lambda}{2NkT}\right) = 1.63 \times 10^5;\ \exp\left(-\frac{f\lambda}{2NkT}\right) = 6.1 \times 10^{-6}$$

For less well-oriented structures N would tend toward smaller values; hence $f\lambda/2NkT$ would be greater than the above estimate.

[2] Whether N_0 should be taken as the number of bonds originally present in a typical square centimeter of cross section, or as a larger number, appears problematic. Evidently, because of cross-linking, stress will not be completely relieved in all segments of a chain once it has been broken at an axial bond. There is a finite probability, therefore, that other axial bonds in the same chain will be broken before at least one such bond in *each* of the chains in a cross section is broken. The rate of bond breakage, as given by Equation 1, is for the whole mass of material, and not for a particular cross section. Breakage across a section is the favored process, however, by virtue of the concept that breakage of one chain increases the force f/N on the nearby chains between cross-links flanking the break. According to the theory underlying Equation 1, the increase of f/N increases the probability of rupture in the overloaded segments of the nearby chains. Rupture of bonds in the cross section more or less defined by the cross-links flanking the original break proceeds with increasing rapidity. The rate dN/dt of bond breakage becomes very quickly mainly that of bonds in the weakened cross section. Reasoning along this line leads to the idea that N_0 should be taken as the average number of bonds (referred to unit cross section) which must ultimately be broken to cause rupture of the specimen, a number slightly greater than the actual average number of bonds/cm.^{2} in the original cross section.

Except for the term $\ln \phi(\nu)$, Equation 6 is substantially that obtained by Tobolsky and Eyring. Three applications of the equation are considered below.

Applications of Theory

For a dynamic fatigue experiment at constant stress-amplitude and frequency, or one under constant load (creep) but at various temperatures, Equation 6 can be written

$$\ln L = \frac{A}{T} + B \tag{7}$$

where

$$A = \frac{F^*}{R} - \frac{f\lambda}{2N_0 k} \quad \text{and} \quad B = -\ln \frac{f\lambda\phi(\nu)}{2N_0 h}$$

Equation 7 is that obtained by Busse, Lessig, Loughborough, and Larrick [1] in their fatigue experiments on cotton, rayon, and nylon tire cords at various temperatures, and by Waller and Roseveare [10] on viscose rayon yarn and cord.

For constant temperature and frequency but various stresses, Equation 6 can be written

$$\ln L = -fC - \ln fC + D \tag{8}$$

where

$$C = \frac{\lambda}{2N_0 kT} \quad \text{and} \quad D = \frac{F^*}{RT} - \ln \frac{kT}{h}\,\phi(\nu)$$

For $fC \geqslant 1$, the right-hand side of Equation 8 is governed largely by the term $-fC$. Hence Equation 8 may be written

$$\ln L = D - fC \tag{9}$$

This again is an equation of the form found by Busse et al. to describe their results—in this case, results of dead-load as well as vibration experiments at constant temperature and strain-amplitude. The dynamic fatigue results of Waller and Roseveare on rayon cords also conform to Equation 9. More recently, Coleman [2, 3, 4] has published results of dead-load experiments on rayon, Dacron,[3] and nylon 66 yarns and filaments confirming Equation 9.

For a vibration test at constant temperature and stress amplitude, Equation 6 may be written

$$\ln L = E - \ln \phi(\nu) \tag{10}$$

[3] Du Pont trademark.

where it may be seen that E is a substitution:

$$E = \frac{F^*}{RT} - \frac{f\lambda}{2N_0 kT} - \ln \frac{f\lambda}{2N_0 h}$$

Let $\phi(\nu)$ be given the form

$$\phi(\nu) = (1 + m\nu)^n \qquad n > 0 \tag{11}$$

which conforms to the requirement $\phi(0) \neq 0$. m is a proportionality factor having the dimensions of inverse frequency (i.e., time). Then Equation 10 may be written

$$L = \frac{\exp E}{(1 + m\nu)^n} = (1 + m\nu)^{-n} \exp E \tag{12}$$

Evidently for sufficiently large values of ν,

$$1 + m\nu \approx m\nu$$

Equation 12 is then experimentally indistinguishable from the expression

$$L = F\nu^{-n} \tag{13}$$

where the new constant $F = m^{-n} \exp E$.

Equation 13 is that deduced by Waller and Roseveare from their fatigue studies on viscose rayon. For two tire cords they get a value of almost exactly 1/2 for n when ν is expressed in cycles per minute.

Discussion

The relationship between the observed temperature dependence of fatigue life of textile materials as expressed by Equation 7 and the reaction rate theory as originally developed has been noted by Busse and co-workers, Tobolsky and Eyring, and Waller and Roseveare. Most of the data considered by these workers, however, are for dynamic experiments involving periodic stresses, whereas the original theory makes no special provision for periodicity in the loading. In the present development leading to Equation 7, though the frequency of stressing is considered to be constant, its possible role is recognized by virtue of its indicated influence on the parameter B.

In the recent series of papers mentioned above, Coleman has developed a theory of fatigue failure in textile filaments which, like the present, is a modification of that of Tobolsky and Eyring. He correctly points out [3] that his theory predicts the observed dependence of fatigue life on temperature, though without deriving the foregoing Equa-

tion 7. Likewise his theory leads to Equation 9[4] for lifetime as a function of steady stress (frequency = 0) [4].

A feature of the Coleman theory is the consideration which has been given to the unique influence of periodic, as distinct from static, loading on the kinetic behavior of the molecular deformation units. In only one other treatment, that of Ree, Chen, and Eyring [8], has an attempt been made to introduce into the reaction rate picture of deformation and rupture a concept reflecting the dependence of mechanical properties on frequency of stressing. The latter authors argue that under periodic stressing the activation free energy is not constant, but becomes a function of frequency,[5] whereas Coleman, considering the applied stress f to be a function of time generally, merely makes it a sinusoidal function for the vibrational case. His development, however, leads to the theorem that whenever the applied stress is periodic and the fatigue lifetime is very much greater than the period of vibration, the lifetime is independent of the frequency. This conclusion is in evident conflict with the above Equation 13. No specific experimental data are cited by Coleman in support of his theorem. The only conclusive published results on the frequency effect in textiles are those of Waller and Roseveare, cited above, for which Equation 13 is the expression. Busse and coworkers conclude from their experiments that if the vibration frequency is over 2.5 times the resonance frequency of the fatigue machine the lifetime is constant. Their results indicate, however, that in general fatigue life is not independent of frequency; lifetime at frequencies above the resonance band is about 50% of the lifetime at frequencies below the band. Using the experimental points which are undisturbed by the resonance effect, and allowing for normal scatter, the results of Busse and co-workers could be represented by Equation 13, though there are not sufficient data to say that such a representation is unique.

[4] It is of interest to note that for the derivation of Equation 9, both Coleman's theory and the present application require that the applied stress, f, be greater than a quantity which may be interpreted as being proportional to thermal energy per unit volume in the rupture region: $2kT/\delta$ (where δ is a "displacement volume") in the first case and $2N_0kT/\lambda$ in the second.

[5] The rather general definition which has been given the function $\phi(\nu)$ in the present development makes it interpretable as effectively a measure of the reduction in the activation energy F^*. This can readily be seen when it is noted that $\phi \equiv \exp \ln \phi$, so that the product $\phi \exp(-F^*/RT)$ in Equation 3 may be written $\exp[-(F^* - RT \ln \phi)/RT]$.

Acknowledgment

To Dr. J. H. Dillon the writer is indebted for profitable discussion of the considerations set forth in this article.

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The Effect of Nuclear Radiation on Fibrous Materials[1]

Part II: Dyeing Characteristics of Irradiated Cotton and Rayon

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Abstract

The dye adsorption characteristics of a series of cotton and rayon samples exposed for different periods of time to gamma rays and to thermal neutrons have been determined. For this work substantive dyes of known behavior toward degraded celluloses were used. The effect produced in the case of neutrons was twofold. At the early stages and again during the later stages of irradiation, the dye adsorption of the samples was increased; at intermediate exposures the adsorption was decreased. Because hydrolyzed cellulose behaves in the former manner and the acidic type of oxidized cellulose in the latter, the data suggest that neutrons have an effect similar to both hydrolysis and oxidation. Gamma rays (CO^{60}), however, gave only the effect of oxidation.

Introduction

The fact that cellulose is readily degraded by gamma radiation and neutron bombardment has been well established. Early workers Seaman, Millett, and Lawton [5] and Charlesby [1] showed that high energy cathode-ray bombardment of wood pulp and cotton linters resulted in chain-scission, as evidenced by a decrease in viscosity and an increase in water solubility. Their work suggests a course of degradation analogous to the hydrolysis of cellulose. Gilfillan and Linden [2] found that the strength of cotton was decreased by gamma irradiation and in a subsequent work [3] proposed that the major cause of degradation was oxidation resulting in the formation of a cellulose peroxide. The work of Teszler, Kiser, Campbell, and Rutherford [6] favors a mechanism involving both hydrolysis and oxidation.

It is reasonable to assume that the physical-chemical changes due to irradiation should affect the dyeing characteristics of cellulose, as some preliminary work by Gilfillan and Linden [3] and Teszler et al. [6] suggests. Moreover, it has been shown that either hydrolysis or oxidation of cellulose alters its dyeing characteristics, particularly with respect to exhaustion [7]. Specially selected dyes show a reduced adsorption on oxidized materials but an increased one on hydrolyzed materials. When carboxyl groups are formed by oxidation, their presence inhibits the uptake of a dye that also contains acid groups, the inhibition increasing as the number of acid groups in the dye increases. On the other hand, the same dyes are adsorbed to a greater extent by hydrolyzed cellulose. Thus, it was believed that an examination of irradiated cellulosic fibers with respect to dye adsorption characteristics might show something concerning the nature of the degradation. It was recognized that hydrolysis (or a similar reaction) and oxidation might occur simultaneously during irradiation, and that the results would reflect only the predominance of one type of reaction over the other at any given period of exposure.

The present work describes the dye adsorption characteristics of a series of cotton and rayon samples exposed for different periods of time to gamma rays alone (Co^{60}) and to thermal neutrons (BNL reactor[2]). The results have suggested, by analogy with materials degraded in a known manner, the general nature of the degradation of cellulose by radiation.

[1] Part I appeared in the October 1956 issue.

[2] Brookhaven National Laboratory.

Materials and Methods

Unscoured and unbleached Deltapine cotton spun into 30's yarn, and unscoured, unbleached 1100 den. high-tenacity rayon yarn were used. The fibers were irradiated with neutrons in the BNL reactor for 5, 50, 100, 500, and 1000 min. in a water-cooled exposure port having a thermal flux of 1.5×10^{12} neutrons/cm.^{2}/sec. The fibers received a total flux ranging from 4.5×10^{14} to 9×10^{16} neutrons/cm.^{2}. Samples of the cotton and viscose yarn were also irradiated in a Co^{60} gamma source (BNL) for 1.02, 10, and 60 hr. The source had a dosimetry of 5×10^5 roentgens/hr. The samples received total doses of 5.1×10^5, 5.0×10^6, and 3.0×10^7 roentgens, respectively.

Cotton samples were also hydrolyzed with 3.5 *N* HCl and 8.0 *N* HCl for 17 hr. at room temperature. Samples of cotton containing carboxyl groups were prepared by oxidation with periodic acid and subsequent treatment with chlorous acid [4].

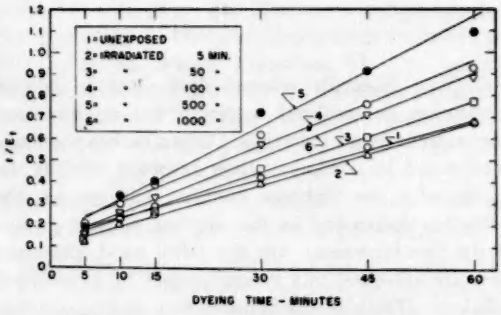

Fig. 1. The exhaustion of Diphenyl Blue BT Conc. on cotton exposed for different periods of time to neutrons.

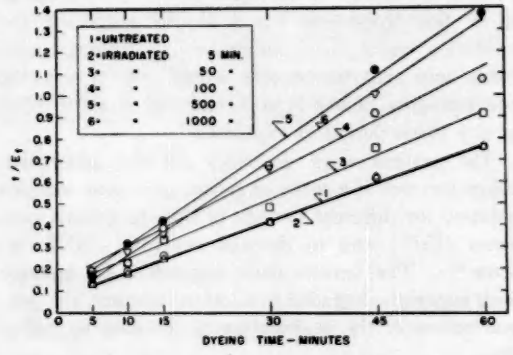

Fig. 2. The exhaustion of Diphenyl Brilliant Blue FF on cotton exposed for different periods of time to neutrons.

One-gram samples were dyed with Diphenyl Blue BT Conc. (Direct Blue 8, CI 24140) and Diphenyl Blue FF (Direct Blue 1, CI 24410) at 90° C. for 1 hr. in a dyebath containing 50 mg./l. of the dye and 5 g./l. NaCl, with a fiber:dyebath ratio of 1:100. Aliquots of 1 ml. were taken after 5, 10, 15, 30, 45, and 60 min. of dyeing and diluted 1:10 for spectrophotometric measurements. The Beckman Model DU Quartz Spectrophotometer was used. The optical densities of the aliquots were converted in terms of mg./l. of dye with the aid of calibration curves.

Results and Discussion

Cotton

As noted above, two dyes were selected for this work—Diphenyl Blue BT. Conc. and Diphenyl Brilliant Blue FF. These have two and four sulfonic groups respectively. When the exhaustion was plotted against the time of dyeing for any given sample, the curve so obtained could be fitted by a second-order equation. This was readily transformed into a straight line by plotting the dyeing time t on the x-axis of the coordinate system and the ratio of dyeing time t to percent exhaustion at t, E_t, on the y-axis. In this manner the comparative rates of dyeing of the various samples were easily obtained.

Figure 1 depicts the rate of exhaustion of neutron-irradiated cotton dyed with Diphenyl Blue BT Conc. Curve 1 represents the untreated material, and Curves 2, 3, 4, 5, and 6 represent samples irradiated in the reactor for 5, 50, 100, and 1000 min., respectively. Several interesting points may be noted. First, one curve falls below, while the others fall above the line representing the exhaustion rate of the unirradiated cotton. Second, the curves are not in a consistent pattern with respect to the degree of exposure. This indicates a difference in dyeing behavior between the irradiated and unirradiated samples and among the irradiated samples themselves. It is obvious that when the rate curve of a treated sample falls below the untreated, the ratio t/E_t is smaller for the treated sample. Since t is constant in all cases, such an observation is caused by an increase in E_t; i.e., an increase in exhaustion. If, on the other hand, the rate curve for an exposed sample falls above that of the untreated sample, t/E_t is increased, and less exhaustion is obtained.

It was previously indicated that the hydrolysis of cotton would result in an increased adsorption of selected dyes, while oxidation would cause a decrease.

Thus, the analysis of the data in Figure 1 leads to the conclusion that the curves below the line representing the untreated material indicate a change in the direction of hydrolysis, while those above the reference line indicate oxidation. It can be seen that Curve 2, representing the sample irradiated for 5 min., falls below the untreated line, while Curves 3, 4, 5, and 6 all fall above the reference line. It should also be noted that Curve 6 falls closer to the reference line than Curves 4 and 5. These results are interpreted to mean that initially and during the first few minutes of exposure, a reaction showing the effect of hydrolysis occurs. As the exposure is continued, an oxidation effect is noted that predominates over the hydrolytic until after prolonged exposure, when oxidation again becomes secondary. In a subsequent paper [6] it will be shown that, during the early periods of exposure to neutrons under the conditions of these experiments, the viscosity of the cotton dropped rapidly while the tenacity decreased slowly. Good retention of strength accompanied by a loss in viscosity is characteristic of some types of oxidation. In this respect, with the exception of the first few minutes, these data are consistent with the dyeing characteristic; i.e., both suggest oxidation as the predominating type of degradation until the later stages of attack. At the dose rates used in this work, 1.5×10^{12} n./cm.^{2}/sec., the "later stages" begin somewhere between 100 and 500 min. This is the point where the degraded material begins to exhibit dyeing characteristics of hydrolyzed cellulose and the effect of oxidation no longer predominates.

Figure 2 shows very much the same, but since the samples here were dyed with Diphenyl Brilliant Blue FF, a dye having four sulfonic groups, the effect of oxidation is more emphatically shown, while that of hydrolysis is minimized. The difference is observed between Curves 1 and 2 which represent, respectively, the untreated and the sample exposed for only 5 min. This difference in the two dyes was observed in every case in this investigation.

A plot of percent exhaustion against time of irradiation should also illustrate the differences in dyeing characteristics of the cotton samples. A curve should be obtained that first rises sharply, then recedes, and finally rises again. Such a curve was indeed obtained, and is illustrated in Figure 3. The initial rise represents an effect similar to hydrolysis; the fall that ensues signifies the hydrolytic type of degradation as the predominating one. The curves

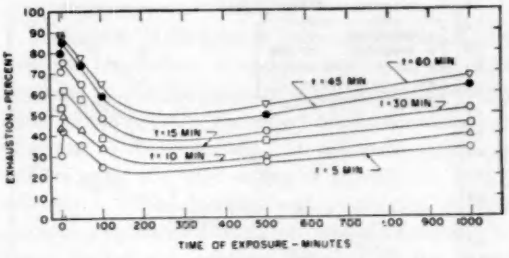

Fig. 3. Effect of neutron irradiation of cotton on exhaustion of Diphenyl Blue BT Conc.; t indicates dyeing time.

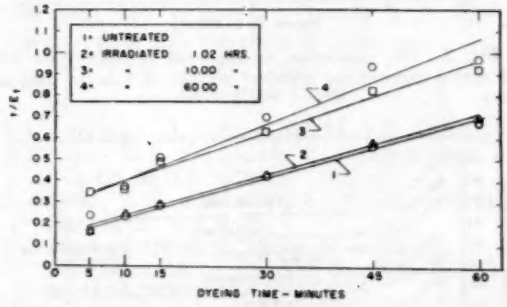

Fig. 4. The exhaustion of Diphenyl Blue BT Conc. on cotton exposed for different periods of time to gamma rays.

were similar irrespective of dyeing time, although there was a tendency toward a minimizing of the initial rise in exhaustion when long periods of dyeing were used.

Samples exposed to gamma radiation were analyzed in a similar manner. The results are shown graphically in Figures 4, 5, and 6. Curve 1 in Figures 4 and 5 represents the untreated cotton, while curves 2, 3, and 4 represent samples exposed for 1.02, 10, and 60 hr., respectively. These data show that in the case of gamma irradiation there is no evidence of an effect similar to hydrolysis; all the rate curves fall above the reference line and thus signify oxidation as the predominating effect. The plot of exhaustion versus time of irradiation (Figure 6) results in a curve that initially decreases rather sharply and then levels off but has a tendency towards a negative slope. Thus, it appears that the effect of gamma radiation is somewhat different from that of neutrons. It should be pointed out that the cotton was highly degraded at the 60 hr. point and was equal in viscosity to the sample exposed for 1000 min. to neutrons.[3] Thus, the dyeing differences

[3] The degree of polymerization was of the order of 80. The initial value was 2488.

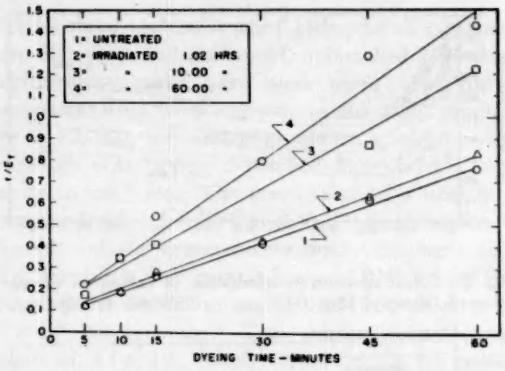

Fig. 5. The exhaustion of Diphenyl Brilliant Blue FF on cotton exposed for different periods of time to gamma rays.

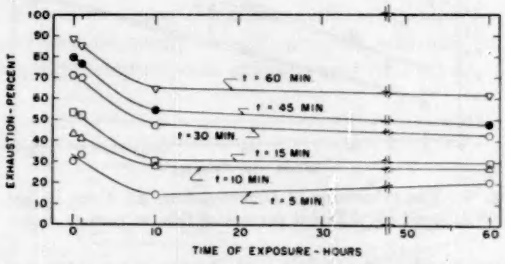

Fig. 6. Effect of gamma irradiation of cotton on exhaustion of Diphenyl Blue BT Conc.; *t* indicates dyeing time.

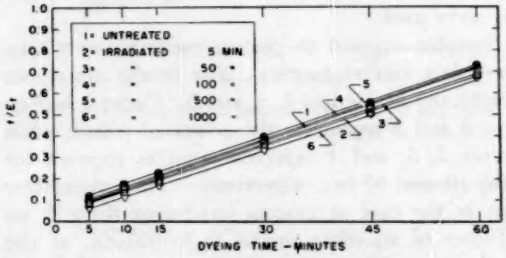

Fig. 7. The exhaustion of Diphenyl Blue BT Conc. on rayon exposed for different periods of time to neutrons.

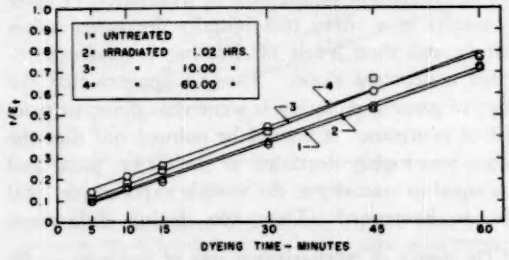

Fig. 8. The exhaustion of Diphenyl Blue BT Conc. on rayon exposed for different periods of time to gamma rays.

among the samples exposed in different ways cannot be attributed to differences in the extent of degradation. As a matter of fact, all the dyeing experiments were carried out on samples of cotton that exhibited the same relationships between viscosity and tenacity after exposure in the reactor and to the Co^{60} source.

The difference between the adsorption of the disulfonated and tetrasulfonated dyes can be seen by comparing Figures 4 and 5. As expected, the latter shows greater differences between the exposed samples.

Rayon

The studies of the irradiated rayon samples yielded the same results as were noted in the case of cotton. The exhaustion-rate curves for neutron-irradiated rayon (Figure 7) show the characteristic initial increase in exhaustion, followed by a decrease, and finally a rise beyond 100 min. of exposure. In contrast to cotton, the rates of dyeing of the irradiated rayon samples were nearly the same (i.e., the slopes of the curves are about the same), but the amount of adsorption differed as a function of the duration of exposure to radiation. The effect is best shown in Figure 9, particularly during the short periods of dyeing. A masking of the decrease in exhaustion is obtained after about 30 min. of dyeing because of the high exhaustion of the dyebath by the rayon. The result of gamma radiation again appears to be one of oxidation predominantly, since only a depression of exhaustion was obtained. The data are shown in Figure 8.

Dyeing Characteristics of Chemically Degraded Cotton

That hydrolysis and oxidation of cotton produce the effects discussed above was confirmed by the dyeing of samples degraded by specific methods.

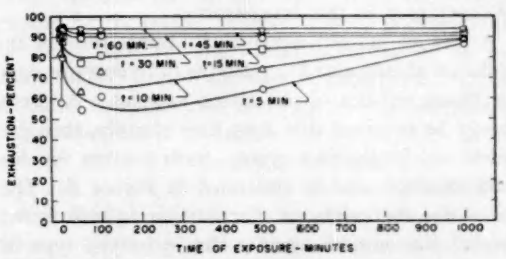

Fig. 9. Effect of neutron irradiation of rayon on exhaustion of Diphenyl Blue BT Conc.; *t* indicates dyeing time.

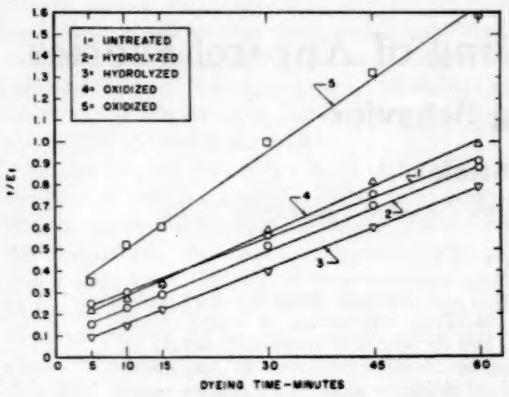

Fig. 10. Effect of chemical degradation of cotton on the exhaustion of Diphenyl Brilliant Blue FF.

The data are shown in Figure 10. Curves 2 and 3 represent samples hydrolyzed to two different degrees, 3 being the most highly degraded. Increased adsorption was obtained. Curves 4 and 5 represent a cotton oxidized so that carboxyl groups were produced at the 2 and 3 position in the anhydroglucose units. The degrees of oxidation of the two samples in terms of total units oxidized were about 1 in 200 (Curve 4) and 1 in 75 (Curve 5). An illustration of the sensitivity of the dyes to these relatively low degrees of oxidation is shown adequately by the decrease in exhaustion.

Conclusions

The results of the present investigation have shown that the irradiation of cotton and rayon by either neutrons or gamma rays alters the dyeing characteristics of the fibers. The effect produced in the case of neutrons was twofold. At the early stages and again during the later stages of irradiation, the dye adsorption of the samples was increased; at intermediate exposures adsorption was decreased. Because hydrolyzed cellulose behaves in the former manner and oxidized cellulose in the latter, the data suggest that neutrons have an effect similar to both hydrolysis and oxidation. Gamma rays (Co^{60}), however, gave only the effect of oxidation.

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Factors Affecting the Drying of Apparel Fabrics[1]

Part I: Drying Behavior

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Abstract

When apparel fabrics made of various natural and manmade fibers are dried under "drip-dry" conditions, the usual constant rate and falling rate periods of drying can be observed. The former is normally the longer, and its length is determined largely by the amount of water which is initially picked up by the fabric and must be evaporated. This depends primarily on the fiber content and the thickness of the fabric. With rayon and cotton fabrics it can be controlled to some extent by treatment with aminoplast resins.

The critical moisture content, which is the water concentration at the end of the constant rate period, has been found in some cases to depend on the sample size and fabric construction when determined on vertically suspended samples. In these cases, it is not related in a simple way to the regain of the fibers in saturated air, as is sometimes proposed.

For hydrophilic fabrics, the whole falling rate period may be characterized by a drying coefficient based on the assumption that the area of free surface evaporation is the rate controlling factor and that this is proportional to the water content. With hydrophobic fabrics, the latter half of the falling rate period is not consistent with this assumption, and the rate becomes somewhat more rapid.

IN recent years there has been an increasing number of fabrics manufactured for use in garments which can be washed quickly and easily by the wearer and worn again with little or no ironing. Such fabrics represent a considerable step in producing fabrics which consumers will find to be more useful and desirable and to require a minimum of effort in their maintenance. The first fabrics of this sort were made entirely from synthetic fibers. Later, blends of synthetic with natural or regenerated fibers were introduced. Most recently, chemical treatments have been developed which give cotton fabrics these "wash and wear" characteristics.

Among the characteristics of synthetic fibers which have encouraged the use of wash and wear procedures with garments made from them is the relatively short time required for drying them after washing. This is a consequence of their hydrophobicity and low water imbibition, but is not necessarily related to the appearance of the garment after laundering. However, quick drying is certainly a convenience that must be considered to be one of the advantages of synthetic fabrics. The present emphasis on wash and wear finishes for cotton makes it desirable to know to what extent chemical finishing treatments will affect the drying behavior of the fabric and what advantages in this respect these new finishing techniques will produce. This paper deals with the drying of fabrics from the saturated state, the process commonly called "drip drying," and is particularly concerned with factors which are important in the drying of garments. Later papers in this series will take up the characterization of the water holding capacity of fabrics and the effect of finishing treatments on water holding capacity.

Drying processes have been relatively neglected as fields for textile research; most of the work that has been done has been primarily concerned with drying after dyeing and finishing operations. However, Fourt, Sookne, Frishman, and Harris [6] have investigated some aspects of drying fabrics under conditions similar to those used for garment drying. They concluded that the major portion of the time required for drying is occupied by the evaporation of liquid water, which takes place at a constant rate per

[1] Presented at the Sixth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., October 2, 1957.

unit of surface area. The rate determining factor is the layer of still air over the fabric surface through which the water must diffuse after evaporation. The rate depends on the temperature, humidity, and movement of this air layer, but not on the construction or fiber content of the fabric.

Coplan [3] has studied a variety of fibers knit in the form of socks to determine the effect of inherent fiber properties on the speed of drying under household conditions. He found that the total drying time was a function of the ratio of total moisture uptake to the surface area of the fabric. He also discussed in detail some of the factors involved in the various stages of drying and reviewed the earlier work in this field where attempts had been made to apply classical drying theory to the drying of textiles.

As Cowen has pointed out in a review of some principles of drying [4], two groups of factors govern drying behavior. One group is comprised of the properties of the material being dried, while the second is made up of the external factors which control the transfer of heat and moisture to and from the fabric. In the present work we have been concerned only with factors of the first sort, and all of the drying experiments have been carried out under a single constant set of drying conditions. The procedure was similar to that used by Fourt and his coworkers. Dripping wet samples have been allowed to dry in the standard atmosphere for testing textiles, 70° F. and 65% R.H. A continuous weight record was obtained by use of the weighing system of an Instron tester [7].

Experimental

The technique used to observe the drying of a fabric under drip dry conditions was as follows. A sample of fabric was prepared as shown in Figure 1 with a copper wire hanger threaded through five small slits along the upper edge. The length was varied to obtain different sample areas. The sample was immersed in a tray of water, and, while it was still immersed, the ring in the center of the wire was placed on a hook suspended from the strain gauge of an Instron tester which had been previously calibrated and balanced to zero with the copper wire alone on the hook. The tray was then lowered, leaving the sample suspended on the hook wet and dripping. Drying was allowed to proceed until the chart record showed that the sample had come to equilibrium. The Instron tester was in a room held at the standard conditions of temperature and humidity for textile testing, and stood in an area of gentle but turbulent airflow produced by the air conditioning equipment. The constancy of these conditions was attested to by the fact that a reproducible drying rate could be obtained over the several months involved in this work.

A typical drying curve is shown in Figure 2, which shows the weight of water in a fabric as drying proceeds. There is a rapid initial loss of weight as liquid water drains from the fabric, followed by a longer period of weight loss at a constant rate. Finally, there is a gradual approach to the equilibrium moisture content at a decreasing rate. This two-stage behavior is normally observed in drying studies [4, 5, 11]. The following data can be derived from a drying curve like that shown:

1. Drained water content. This is obtained by extrapolating the period of steady weight loss back to zero time.

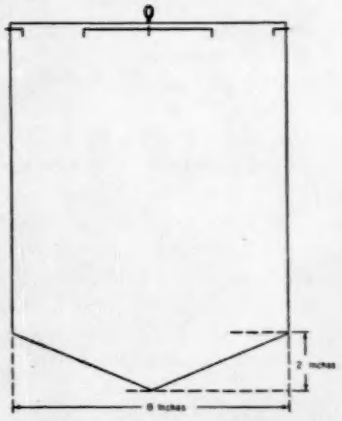

Fig. 1. Sample for drying test.

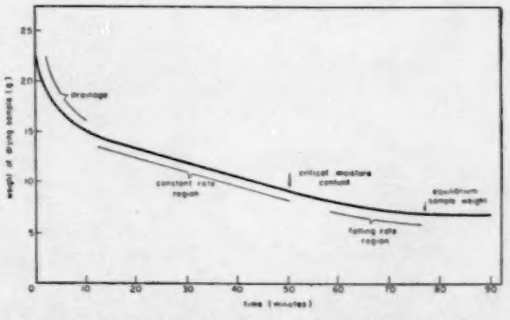

Fig. 2. Typical weight-time curve for drying fabric.

2. Drying rate during constant rate period. This is obtained from the slope of the drying curve during the period of steady weight loss.

3. Critical moisture content. This is defined as the moisture content of the fabric at the end of the constant rate period when the slower approach to equilibrium begins.

4. A drying coefficient characteristic of the falling-rate period. This is the slope of the line obtained by plotting the log of the relative moisture content against time for the period after the critical moisture content is reached.

5. Total drying time. This can be divided into two parts, the time to reach the critical moisture content and the time of the falling rate period.

6. Equilibrium moisture content. This cannot be determined very accurately from the drying curve, but it is useful as a check on the stability of the load weighing system.

These quantities are comparable to those commonly used in chemical engineering studies of drying in chemical processes [9].

Drying tests were made on different sized samples of a number of fabrics of varied fiber content and construction; they are listed in Table I. All of the fabrics were undyed. The rayon, cotton, and wool fabrics were used as received in the mill-scoured state. The synthetic fabrics were rescoured in 0.01% Triton X-100. Tests were also made on cotton sheeting and rayon challis samples treated with different amounts of an ethylene urea-formaldehyde precondensate (Rhonite R-1) and of a straight urea-formaldehyde precondensate of the type long used for crushproofing rayon (Rhonite 610).

Results and Discussion

The data obtained are collected in Tables II and III.

The theoretical aspects of drying processes are reviewed by Cowen [4] and by Marshall and Friedman in Perry's handbook [9]. There are usually two well-defined stages in drying as indicated above, one in which water is being removed at a constant rate and a second during which the rate of water removal constantly falls. During the constant rate period, the rate is determined by the diffusion of water vapor from the saturated surface of the material through a stationary air film into the air stream. In the absence of radiative heat transfer, this rate depends entirely on the conditions of temperature, humidity, and air flow around the sample, and no characteristic of the sample itself is concerned. The rate of drying in the constant rate period is given by

$$\frac{dw}{dt} = \frac{hA\,\Delta T}{\lambda} = K_g A\,\Delta P$$

where h is the total heat transfer coefficient, A is the area, λ is the latent heat of evaporation of water at the temperature of the drying material, K_g is the mass transfer coefficient, $\Delta T = T_a - T_s$, where T_a = air temperature and T_s = temperature of drying surface, and $\Delta P = P_a - P_s$, where P_a = partial pressure of water in the air and P_s = vapor pressure of water at T_s.

When the heat transfer involves convection only, as it does in the present case, T_s is the wet-bulb temperature of the air and P_s is the vapor pressure at this temperature. From this equation it is obvious that factors like the rate of water movement

TABLE I. Fabrics Used in Drying Tests

Fabric	Fiber	Weight, mg./cm.²	Thickness, mm.	Ends/in.	Picks/in.
Printcloth	Cotton	15.97	.25	84	78
Sheeting	Cotton	16.73	.39	54	46
Lawn	Cotton	8.51	.20	107	97
Challis	Spun rayon	20.31	.32	84	64
Challis	Spun nylon	16.91	.32	74	68
Challis	Spun Dacron*	13.01	.35	55	52
Flat, plain weave	Filament nylon	4.70	.16	116	80
Flat, plain weave	Filament Dacron*	4.14	.18	104	108
Botany flannel	Wool	46.88	.79	54	44

* Du Pont trademark.

within the fabric or the nature of the fabric surface can have nothing to do with this rate. This is demonstrated by the constancy of the drying rate obtained in this experiment for widely different fabrics, and its constancy further shows that the drying conditions used over a period of six weeks or so were comparable. The average drying rate found for 57 tests was 2.24×10^{-4} g./cm.^{2}/min. This corresponds to a heat transfer coefficient of 1.87×10^{-2} cal./min./cm.^{2}/deg. (The latter is calculated on a drying surface equal to

TABLE II. Drying Tests on Apparel Fabrics

Fabric	Area, in.^{2}	g./g. Drained water content	g./g. Critical water content	g./g. Equil. moisture content	Constant drying rate, g./min./cm.^{2} $\times 10^4$	Drying coeff. $\times 10^2$	Drying time, min. Constant rate	Drying time, min. Falling rate	Drying time, min. Total
Cotton printcloth	40	1.72	.241	.085	2.64	3.44	35	12	47
	80	1.64	.230	.091	2.42	3.44	69	10	79
	100	1.61	.363	.079	2.23	2.92	54	21	75
	110	1.76	.407	.101	2.72	3.02	48	19	67
	110	1.59	.333	.096	2.00	2.57	62	19	81
	140	1.55	.423	.107	2.46	2.95	45	25	70
	140	1.62	.512	.101	2.08	1.99	51	33	84
Cotton sheeting	50	1.61	.286	.087	2.54	2.49	78	19	97
	80	1.54	.291	.085	2.54	2.29	83	21	104
	110	1.54	.320	.092	2.51	1.97	84	27	111
	140	1.61	.504	.109	2.37	1.55	76	37	113
Cotton lawn	60	1.25	.348	.084	2.56	3.64	38	17	55
	90	1.23	.361	.088	2.38	3.33	39	18	57
	120	1.25	.376	.091	2.40	3.08	38	19	57
Wool flannel	60	3.18	.398	—	2.30	—	222	—	—
	90	2.61	.603	.152	2.19	1.01	202	40	242
	120	2.34	.429	.150	2.22	0.96	158	48	206
	150	2.27	.313	.171	2.03	0.64	203	40	243
Rayon challis	60	2.03	.559	—	2.12	1.72	72	33	105
	90	2.03	.485	.163	2.03	1.64	77	27	104
	120	2.01	.490	.182	1.86	1.45	81	28	109
	150	1.96	.578	.145	2.09	1.65	68	40	108
Spun nylon challis (unscoured)	60	1.20	.248	.044	2.35	3.55	47	14	61
	90	1.15	.281	.060	2.19	3.10	44	19	63
	120	1.16	.301	.053	2.16	2.69	44	22	66
	150	1.20	.382	.045	2.15	2.26	39	31	70
Spun nylon challis	60	1.26	.216	.047	2.25	3.58	52	13	65
	80	1.24	.316	.042	2.31	3.48	45	18	63
	120	1.22	.386	.035	2.21	2.04	38	31	69
	150	1.21	.362	.052	2.05	1.84	46	36	82
Spun Dacron challis	60	0.86	<.08	.014	2.30	—	—	—	(60.6)
	90	0.83	<.08	.011	1.93	—	—	—	(58.9)
	120	0.84	.275	—	2.26	2.66	38.2	28.2	66.4
	150	0.84	.223	.014	2.10	2.45	46.3	29.8	76.1
Nylon filament	60	0.51	—	.026	2.33	—	—	—	(20)
	90	0.46	.107	.032	2.27	8.50	15	7	22
	120	0.53	.095	.016	2.14	7.94	19	9	28
	150	0.49	.146	.030	2.27	7.14	14	10	24
Dacron filament	60	0.60	~.139	.018	2.38	—	—	—	(21)
	90	0.56	~.083	.005	2.08	—	—	—	(24)
	120	0.52	~.063	.007	2.00	—	—	—	(23)
	150	0.57	~.120	.010	2.04	—	—	—	(24)

twice the fabric area. The drying rate quoted just previously and those in the tables are based on fabric area.)

The time for drying in the constant rate period under constant drying conditions is therefore determined by the amount of water to be evaporated. This depends on the water holding capacity of the fabric and on the critical moisture content. The average values for these quantities are given in Table IV for the various fabrics tested. The initial water holding capacity of a fabric is independent of sample size [2] but depends on both the fiber content and the fabric structure. For example, there are significant differences between the cotton lawn and printcloth and between the spun and filament synthetic fabrics. In the work at Harris Research Laboratories [6], the feature of fabric structure which was found to be correlated with water holding capacity was its thickness. This is confirmed by the present work. The data for our three cotton fabrics fall on the line obtained for 12 fabrics by Fourt and co-workers.

These considerations lead to the conclusion that for samples of equal area and weight the time of drying for the constant rate period is proportional to the difference between the second and third column of Table IV. The fabrics tested would be ranked in the following order:

Quickest drying	Dacron [3] filament	.37
	Nylon filament	.38
	Dacron challis	.74
	Cotton lawn	.99
	Nylon challis	1.12
	Cotton sheeting	1.33
	Cotton printcloth	1.39
	Rayon challis	1.48
Slowest drying	Wool flannel	2.22

The time required for drying in the constant rate period in a practical situation other than drip drying will be determined by the degree of preliminary dewatering produced by padding, squeezing, centrifuging, etc.

The effect of any chemical finishing treatment on the drying time under drip dry conditions must be primarily on the initial water content if a large change is to be expected. The effects of Rhonite R-1 on cotton and rayon and of Rhonite 610 on rayon are shown in Table III and in Figure 3. In the latter, the initial water uptake in grams per gram of treated fabric is plotted against the resin application concentration. If these data were calculated as grams per square centimeter or grams per gram of cellulose, the changes observed would be

[2] The data for wool indicate that the drained water content may be higher for smaller samples. The statistical significance of this trend is not known.

[3] Du Pont trademark.

TABLE III. Drying Tests on Resin Treated Cellulosic Fabrics

Fabric*	Treatment†	g./g. Drained water content	g./g. Critical water content	g./g. Equil. moisture content	Constant drying rate, g./min./cm.^{2} $\times 10^4$	Drying coeff. $\times 10^2$	Drying time, min. Constant rate	Drying time, min. Falling rate	Drying time, min. Total
Cotton printcloth	Untreated	1.64	.324	.081	2.15	3.04	62	15	77
	4.5% Rhonite R-1	1.43	.275	.067	2.15	4.06	56	13	69
	9.0% Rhonite R-1	1.38	.219	.061	2.05	4.55	60	12	72
	13.5% Rhonite R-1	1.32	.150	.052	2.22	5.81	56	8	64
	18.0% Rhonite R-1	1.24	.146	.043	2.19	6.00	54	7	61
Rayon challis	Untreated	2.14	.467	.062	(1.43)	1.63	118	47	165
	10% Rhonite R-1	1.47	.356	.127	2.19	2.33	56	19	75
	20% Rhonite R-1	1.23	.290	.083	2.15	2.70	53	19	72
	30% Rhonite R-1	1.10	.298	.074	2.25	2.98	47	20	67
	40% Rhonite R-1	1.02	.308	.100	2.17	2.83	45	19	64
Rayon challis	17.5% Rhonite 610	1.71	.362	.214	2.19	1.45	67	14	81
	35.0% Rhonite 610	1.58	.362	.150	2.48	2.46	54	17	71
	52.5% Rhonite 610	1.08	.204	—	(1.49)	2.14	79	—	—

* All samples had an area of 100 in.^{2}

† Concentrations are percent solids in treating bath.

somewhat smaller. The change in equilibrium water content is also given in this figure. For cotton, the net change in the amount of water which has to be removed by drying is fairly small, but there is a considerably larger change for rayon. With both fabrics, the total time required for drying can be made as short as that required for spun nylon challis of equal size and weight or for slightly heavier spun Dacron. In filament form, however, both synthetic fibers dry much more quickly.

The critical moisture content has sometimes been identified with the moisture content in equilibrium with a saturated atmosphere [1, 4, 6, 10], and the values listed in Table IV are reasonably close to those expected on this basis, although comparative data for regain at 100% relative humidity are not always reliable. However, it is obvious from Table II that with the cotton and nylon fabrics the observed critical moisture content depends upon the sample size and, in the case of the nylon, the fabric construction. These data are plotted in Figure 4; the critical moisture content given in Table IV for these fabrics is the extrapolated value at zero area. The extrapolated value for the cotton fabrics is quite uncertain, and the plotted data suggest that perhaps it would be better to put separate lines through the points for each fabric. However, this has not been done.

The dependence of the critical moisture content on sample size observed here brings out a complication that was not recognized by earlier workers. This is that there is a fairly considerable concentration gradient for the moisture in the vertically suspended samples. It is set up immediately and persists until the sample is almost dry. The gradients at various times in drying samples of cotton sheeting and Dacron challis are shown in Figure 5. These were obtained by quickly slicing up drying samples and determining the moisture content of the slices by oven drying. With this state of affairs in the sample it is obvious that a critical moisture content at any time during drying is not characteristic of the fiber alone but depends on the vertical height of the fabric sample; only when this difficulty has been eliminated should the relationship of an observed critical moisture content to the regain at 100% R.H. be considered. Others ([12], p. 655) have also pointed out

TABLE IV. Water Content of Fabric at Various Stages of Drying

Fabric	Water content, g./g.		
	Initial	Critical	Equilibrium
Cotton printcloth	1.64	0.25	.094
Cotton sheeting	1.58		.093
Cotton lawn	1.24		.088
Rayon challis	2.01	0.53	.163
Wool flannel	2.60	0.38	.158
Nylon challis	1.24	0.12	.047
Nylon filament fabric	.50		.026
Dacron challis	.84	0.10	.013
Dacron filament fabric	.47		.010

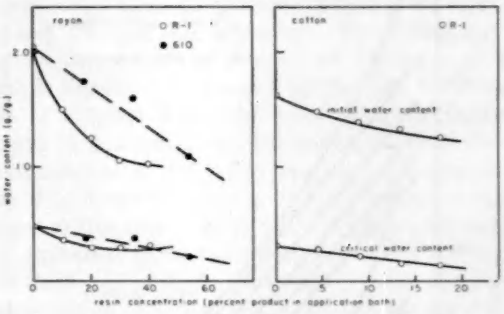

Fig. 3. Effect of resins on initial and critical water contents of cellulosic fabrics.

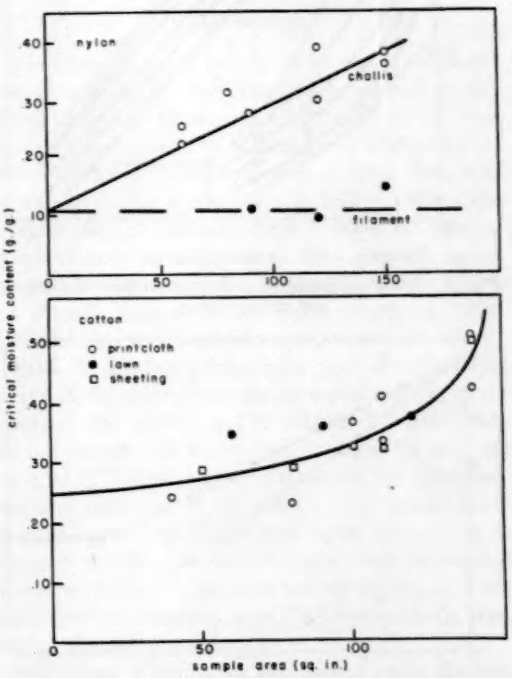

Fig. 4. Dependence of critical moisture content on sample size for nylon and cotton fabrics.

that in general the critical moisture content depends on more than the chemical nature of the drying material. Nevertheless, as far as the actual drying behavior is concerned, the critical moisture content is reasonably well defined as the end of the constant rate period.

When a drying material reaches its critical moisture content, its surface is no longer able to supply enough free water to saturate the air in contact with it. Under these conditions, the rate determining step may be either the transfer of moisture from the inside of the material to the surface or its evaporation from the surface. The rate gradually falls to zero as the equilibrium moisture content is approached. Earlier mathematical treatments of the falling rate period [2, 8, 11] are not directly applicable to the vertically inhomogeneous specimens obtained in this work. We have found, however, that the falling rate period may be characterized for most of these fabrics by a fairly simple equation. While it must be classified as empirical, it can be rationalized to some extent in a way similar to that given by Sherwood [11] for the approximate analysis of practical drying problems. Assume that the rate of water evaporation is directly proportional to the water content of the fabric and inversely proportional to its thickness and to a resistance factor. The latter may be due to diffusion, capillary movement, or surface evaporation. This assumption may be stated as

$$-\frac{dW}{dt} \sim \frac{W}{lr}$$

Integration between the limits of W_{crit} and 0, neglecting shrinkage and any change in r, gives

$$\ln (W/W_{crit}) = t/lr = Kt \qquad (1)$$

where K is the drying coefficient. This equation reasonably well describes the falling rate period behavior observed with the hydrophilic fibers, cotton, rayon, and wool. Some plots of data for typical cotton curves are shown in Figure 6. The fit with the nylon and Dacron fabrics is much poorer, and the deviation is quite marked as equilibrium is approached, as can be seen in Figure 7. In these cases,

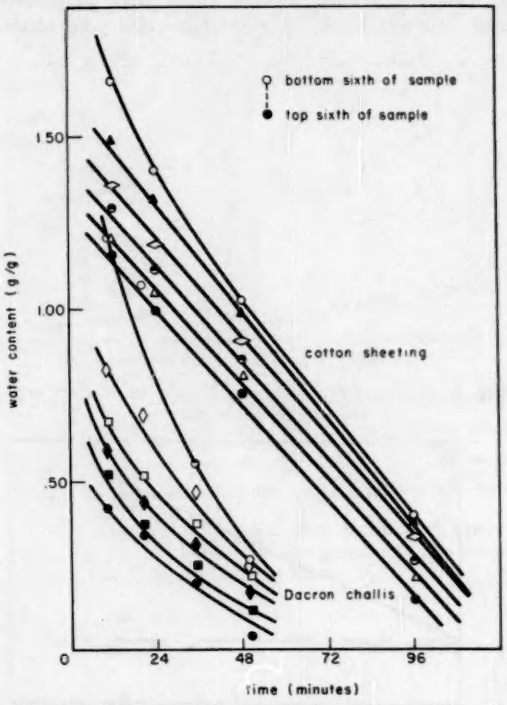

Fig. 5. Moisture gradients in drying samples of Dacron and cotton fabric.

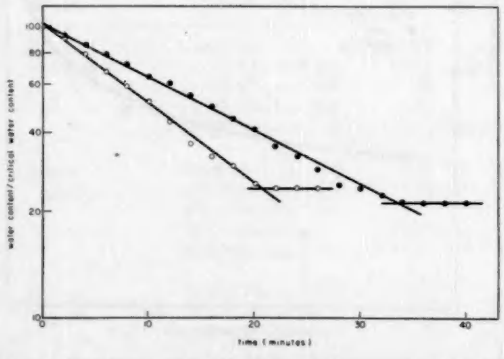

Fig. 6. Drying curves for cotton sheeting samples of different area during the falling rate period.

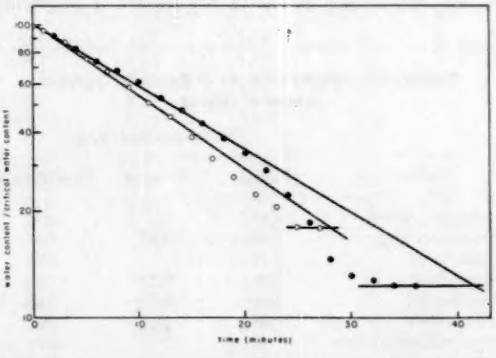

Fig. 7. Drying curves for nylon challis samples of different area during the falling rate period.

the values of K have been calculated from the initial slopes of the lines as drawn in the figure. In determining the time required for the falling rate period, the end point has been taken as the intersection of the sloping line with the equilibrium line, as shown in Figures 6 and 7. This neglects the deviation observed with synthetic fabrics and makes the measured drying time somewhat longer than it actually should be.

The deviation of the synthetic fabrics from Equation 1 is not unexpected, since Sherwood [11] and others (*cf.* [4]) have found that the falling rate period may be divided into two parts and that the rate is linearly proportional to the water content in only the first of these subperiods. The latter assumption is the basis of Equation 1. As can be seen in Figure 6, there is usually a tendency even for cotton fabric to show slight deviations toward the end of the falling rate period, and similar small deviations were observed for rayon and wool. It is presumed [4] that in the first of these falling rate subperiods the rate is determined by the changing resistance to surface evaporation, which is due to the decreasing area of effective evaporative surface; in the second it is determined by the movement of water from within the material to the surface. On this basis our results would indicate that diffusion or other water transfer mechanisms do not become effective rate controlling processes in the case of hydrophilic fibers, but do so for hydrophobic fibers.

When resistance to surface evaporation is the controlling factor, it can be shown ([12], p. 652) that the drying coefficient should be proportional to the reciprocal of the thickness of the material. This appears to be true for the cotton fabrics we have studied. This is demonstrated in Figure 8, where data for 100-in.^{2} samples as read from the lines in Figure 9 are plotted along with values determined directly on multiple layers of print cloth sewn together.

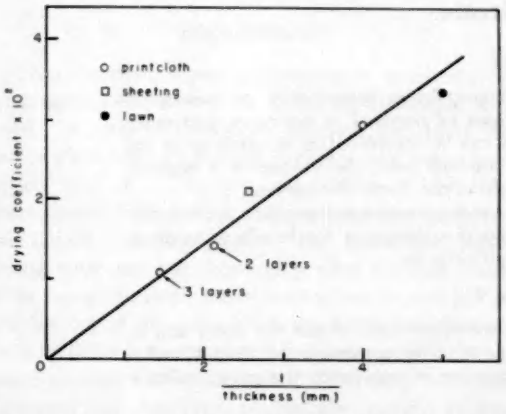

Fig. 8. Relation of drying coefficient to fabric thickness for three cotton fabrics.

The drying coefficient as we have determined it depends upon the fiber content, construction, and sample size of the fabric. In general, lower coefficients were obtained at larger sample sizes, representing a slower rate of drying. The drying coefficients for the cotton samples are plotted against area in Figure 9. The values for the three materials are at different levels, the lawn being the fastest drying in this period and the sheeting slowest. The time involved in this falling rate period is from 25 to 50% of the total drying time under our conditions, so that this effect of fabric structure can have an appreciable effect on the total drying time. When the fabric is partially dewatered by centrifuging, squeezing, or wringing, this period will become relatively more important.

Conclusions

The time required for the drip drying of textile fabrics may be divided into the two usual periods found in drying processes. One is a period when the fabric is drying at a constant rate determined by the conditions of its environment, while in the second the rate of drying is continuously falling. The water concentration at the end of the first period (the so-called critical water content) may depend on the sample size for vertically suspended fabrics and is not directly related to the water regain at 100% R.H., as has sometimes been proposed.

With most fabrics, the greater part of the time required to dry them from the saturated state is in the constant rate period, and its length depends chiefly on the amount of water initially held by the wet material. This depends primarily on the fiber content and thickness of the fabric. The initial water holding capacity of cotton and rayon fabrics can be changed significantly by treatment with aminoplast resins, so that the time required for drying is of the same order of magnitude as that for synthetic fiber fabrics of equal thickness.

The length of the falling rate period under the conditions used here depends upon the fiber content and construction of the fabric and upon the sample size.

The latter is probably due to the nonuniform water distribution in the vertical samples. With hydrophilic fabrics, the falling rate probably is controlled only by the changing effective area for surface evaporation. With hydrophobic fabrics, the second part of the falling rate period may be limited by transport of water from the inside of the material to the surface.

Acknowledgment

The experimental part of this work was carried out by Mrs. Angela Simonson.

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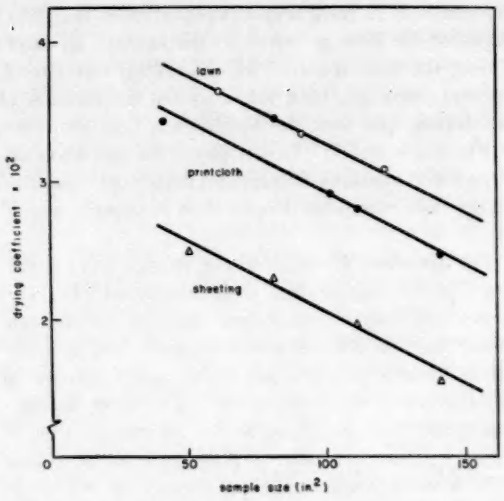

Fig. 9. Relation of drying coefficient to sample size.

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Part II: Capillary Size Distribution

Richard Steele

Abstract

The water holding capacity of a fabric is important in determining its pick-up of treating solutions, the amount of water which must be removed in drying it, and other aspects of its functional behavior. This capacity can be considered to be made up of the volume of a bundle of continuous capillaries of various radii, the volume of a noncontinuous capillary system, and the sorption capacity of the fibers themselves.

A vertically suspended wet fabric develops a water concentration gradient from top to bottom which can be used to calculate the pore size distribution of the bundle of continuous capillaries. The water gradient is given empirically by

$$W_h = a + be^{-kh}$$

where W_h is the water content at height h, a is the water held within the fibers and in noncontinuous capillaries, b is the maximum capacity of the continuous capillaries, and k is a constant which depends on the fabric. The number of capillaries of a given radius r is given by

$$f(r) = \frac{2ab\rho_2\nu \cos\theta}{\rho_1 g\pi}\left(\frac{1}{r^4}\right)\exp\left(-\frac{2b\nu\cos\theta}{\rho_1 g r}\right)$$

where ρ_2 is fabric density in g./cm.^{2}, γ is the surface tension of water in dynes/cm. and θ its contact angle with the fiber, ρ_1 is the density of water, and g is the gravitational constant. This is approximately a log normal distribution.

For cotton printcloth, wool flannel, and nylon challis, the maxima in the radius frequency distributions were found to be 11.1, 19.3, and 9.3 microns respectively.

THE drying of textile fabrics is an important step in wet finishing processes and in the laundering of apparel and other household and industrial articles. The total heat required to dry a fabric or the time required to dry it under a given set of conditions depends primarily on the amount of water which must be evaporated. This water may be held in the wet fabric within the fibers or in the open spaces between them. The part in the interfiber spaces normally accounts for the greater part of the water held. The amount held this way depends very much on the fabric structure, its thickness [1], and any dewatering process such as squeezing or centrifuging which may have been used. It depends also on factors such as the surface tension of the impregnating solution and its contact angle on the fiber surface; this makes it possible that to some extent the extrafiber water holding capacity of a fabric might be controlled by chemical treatment.

This paper describes a procedure for characterizing the water holding capacity of a fabric in terms of a capillary bundle model. It is based on the measurement of the water concentration gradient which is set up when a wet fabric is hung vertically. Data from such measurements can be interpreted in terms of water held (1) in a continuous capillary system, (2) in a noncontinuous capillary system, and (3) within the fibers.

Experimental

To determine water concentration gradients in suspended wet fabrics, the following technique was used. A strip of fabric 3 × 100 cm. was hung inside a glass tube 45 mm. in diameter in a room kept at 20° ± 1° C. The top and bottom of the tube were closed with rubber stoppers and the tube was lined with wet filter paper. The fabric and paper lining were wet out thoroughly with distilled water after being inserted; a reservoir of water was left in the bottom of the tube. The concentration gradient became quite constant after 8 hr., but normally 24 hr. were allowed for equilibration. The strip was then removed and analyzed by quickly cutting it into 15-cm. sections which were weighed in weighing bottles, dried, and reweighed. The bottom 2 cm. of fabric was discarded. The gradient curves obtained in this way for a cotton printcloth, a wool flannel, and a nylon challis are shown in Figure 1. These curves can be fitted with equations of the form

$$W_h = a + be^{-kh} \qquad (1)$$

where W_h is the water content at height h and a, b, and k are constants. The lines in the figure have been calculated from this equation using the values of the constants shown in Table I.

Theoretical

As mentioned above, it has been assumed that water in a vertical wet fabric can be held in three ways. First, there is water imbibed within the fibers themselves. Second, there is liquid water held in limited, noncontinuous capillary systems, such as those formed where two fibers touch each other. Droplets of liquid held this way in filter beds have been referred to as pendular rings by chemical engineers. Third, there is the water held by capillarity in interfiber channels which are essentially continuous. The height to which water rises in such a channel will depend on its effective radius and the other factors in the capillarity equation. Since the latter would be constant for a given system, it seems reasonable to assume that the water concentration gradient set up in a vertical fabric results from a distribution of channel radii in this continuous capillary system.

TABLE I. Frequency Distribution for Capillary Radii in Fabrics

Parameter	Cotton printcloth	Wool flannel	Nylon challis	Units
ρ_2	.016	.047	.017	g./cm.^{2}
a	.62	.42	.20	g./g.
b	1.28	3.44	.94	g./g.
k	.030	.052	.025	
$\cos\theta$	1	1	.34	
$f(r)_{max}$	11.1	19.3	9.29	microns
A	.0104	.0808	.0080	cm.^{2}/linear cm.

The terms in Equation 1 can be identified with the parameters of this capillary model. The second term is the water held in the continuous capillaries, since it is the only term dependent on h. Then b is the maximum capacity of this system at $h = 0$. The first term, a, is then the sum of the water in the non-continuous capillaries and within the fiber; the latter can be estimated from the regain in saturated air. This is usually the smallest factor involved, so that even though reliable data are difficult to obtain the error is not too serious.

The form of the frequency distribution for the continuous capillaries can be calculated in the following way. Let $f'(r)$ be the number of capillaries in a sample of fabric weighing 1 g. per unit of vertical length. Then per unit length

$$dv = \pi r^2 f'(r)\, dr$$

where v is the volume of water in the continuous capillary system and r is the capillary radius. The latter is related to h, the height in the fabric, by the capillarity equation,

$$r = (2\nu \cos \theta)/\rho_1 g h$$

Letting $c = (2\nu \cos \theta)/\rho_1 g$, the capillarity equation can be simplified to $h = c/r$. Then

$$dV = \int_0^{c/h} \pi r^2 f'(r)\, dr\, dh \qquad (2)$$

where V is the total volume.

By differentiating the second term of Equation 1, we obtain

$$\frac{dV}{dh} = -bk \exp(-kh)$$

which may be combined with Equation 2 to give

$$\frac{dV}{dh} = \int_0^{c/h} \pi r^2 f(r)\, dr = -\rho_2 bk \exp(-kh)$$

where ρ_2 is the density of the fabric per cm.^{2} and $f(r)$ becomes the number of capillaries per cm. of fabric width. Integration of this gives the number of capillaries of a given size as a function of their radius.

$$f(r) = \frac{2bk\rho_2 \nu \cos \theta}{\rho_1 g \pi} \left(\frac{1}{r^4}\right) \exp\left(\frac{-2k\nu \cos \theta}{\rho_1 g r}\right) \qquad (3)$$

The first term of Equation 3 which involves r, $1/r^4$, will decrease rapidly as r increases, while the exponential term will increase with r. The distribution curve therefore will be expected to have a maximum.

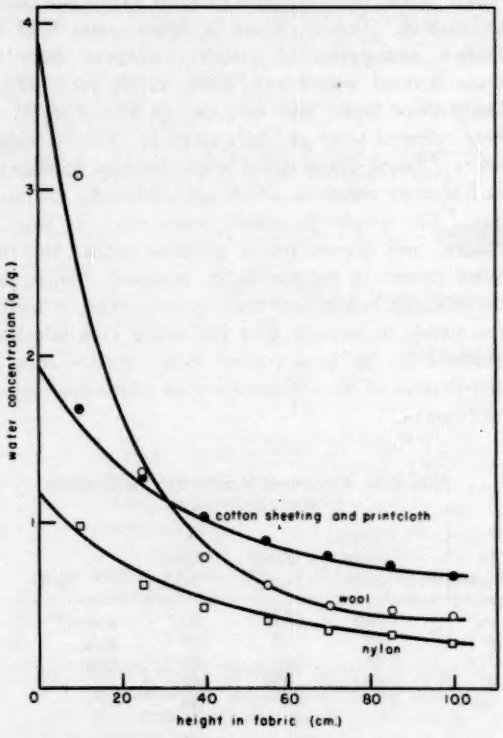

Fig. 1. Water concentration gradients in vertical wet fabrics.

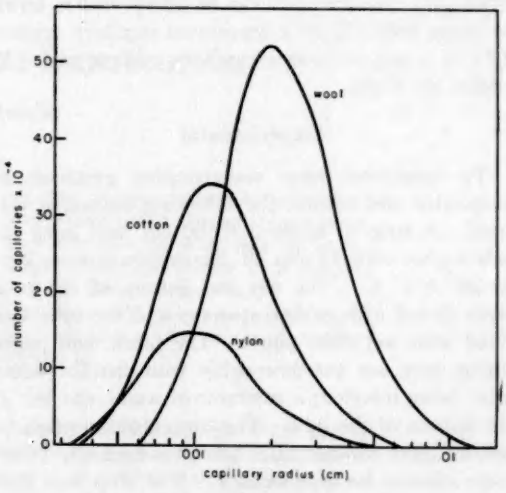

Fig. 2. Calculated frequency distributions for capillary radii.

The distribution curves for the cotton, wool, and nylon fabrics were calculated from the parameters in Table I and are plotted in Figure 2; the shape of the curves is very nearly that of the log normal error curve. The maxima occur at radii which are of the same order of magnitude as those of the fibers themselves; the maxima may be calculated by differentiating Equation 3 with respect to r. It is then found that the most frequently occurring capillary size is that which has a radius of $(b\nu \cos \theta)/2\rho_1 g$. The calculated radii are also given in Table I.

The total area of the continuous capillary spaces is

$$A = \int_0^\infty f(r)\pi r^2 \, dr$$

Substituting Equation 3 for $f(r)$ and integrating, we find

$$A = \frac{b\rho_2}{2}$$

The calculated areas are given in Table I. For cotton printcloth the area calculated is 42% of the dry cross-sectional area of the fiber. The values for wool and nylon are 25 and 97% respectively. The fabric thickness was measured under a pressure of approximately 1 lb./in.^{2}.

Discussion

Experiments similar to those described above have been carried out by Voyutsky and Peregudova [2]. These authors were concerned with the accessibility of the interior of fabrics to latexes and other dispersions, and for this reason wished to characterize the pore size of fabrics. They investigated a cotton kersey and used methanol as the liquid. They equilibrated the samples both from saturation by downflow and from upward wicking. They also used a capillary bundle model, but did not use an analytical expression like the one derived above. They simply calculated the number of capillaries necessary to account for the liquid held in each segment of the test strip. The distribution curves obtained in this way are quite similar to those in Figure 2; their results are plotted in Figure 3. The curve obtained by the wicking procedure is only about $\frac{1}{4}$ as big as that from the downflow experiment. The maxima in the two curves do not occur at the same place, but are in the same range as those we obtained. Voyutsky and

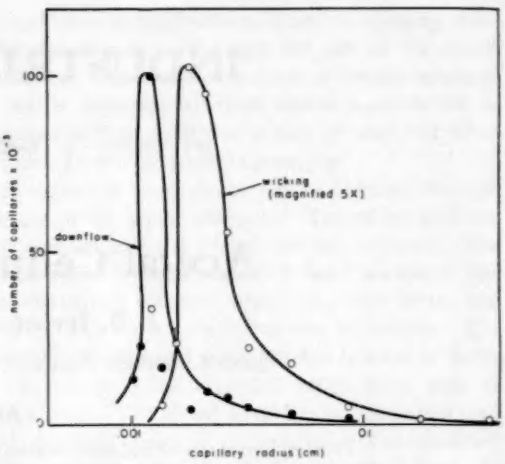

Fig. 3. Frequency distributions of capillary radii in cotton kersey as determined by Voyutsky and Peregudova.

Peregudova did not take into account the possibility that liquid might be held within the fibers or in noncontinuous capillaries. It may be hard or impossible to fill the noncontinuous capillaries by wicking, and this may account for the difference between the results with their two techniques.

Conclusion

The analytical expression derived from the capillarity equation and the empirical equation describing the water concentration gradient in wet fabrics leads to a characterization of the fabric in terms of a capillary size distribution that appears to be very reasonable. The shape of the distribution is approximately log normal. For cotton printcloth the maximum was at a radius of 11.1 microns. For wool flannel and nylon challis, the maxima were 19.3 and 9.3 microns respectively.

Acknowledgment

Dr. Serge Gratch very kindly gave help in some of this work.

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INDUSTRIAL SECTION

Acetal Cellulose Reactants[1]

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Abstract

Three types of acetal cellulose reactants are discussed. Two are in commercial use and one is in the development stage. A general description of the nature of their reactions with cellulose is followed by an analysis of the data obtained from the laboratory evaluations of mill processed fabrics.

The acetal cellulose reactants are a group of materials which produce non-chlorine retentive dimensional control and a wide variety of hand effects including softness, permanent stiffness, and a range of crease resistances.

UREA derivatives have been used for years in the textile industry. They have been applied to a large and still increasing volume of fabrics. However, they suffer from certain disadvantages, and it is only natural that chemical manufacturers have poured considerable research effort into developing products which get around some of those drawbacks.

One of the serious shortcomings of urea derivative chemicals is the fact that chlorine bleaching of treated fabrics permits chloramine formation. Subsequent heating by ironing results in the release of hydrochloric acid, which weakens and discolors the fabric. This property of chlorine retention by treated fabrics has been the cause of a growing volume of discussion and a considerable amount of fabric finishing experimental work. The outcome of one such research and fabric finishing program on this subject is a group of products which may be termed acetal cellulose reactants.

Discussion

Acetals are rather easily prepared derivatives of aldehydes. They can be made from two moles of an alcohol and one mole of aldehyde in the presence of an acid or metal halide catalyst.

Two kinds of acetal cellulose reactants are to be discussed here.

The first are rather simple polymeric acetal condensation products. Under conditions of textile fabric curing these products may be said to fragment and form cross-links by transacetalization. A typical polymeric acetal condensation product is depicted in Figure 1.

Hereafter products of this type will be referred to as "glycol acetals" and modifications thereof will be designated as "modified glycol acetals."

The second kind are groups of materials capable of forming the above described cross-links and of forming polyacetal polymers within the fiber. A typical such material will be termed a pentaerythritol acetal.

Patents covering products, processes, and some of the formulations to be cited here are pending or issued in the United States, Canada, and major foreign countries. Up to now the major portion of the practical fabric finishing with acetals has been done with members of the first group; most of the data presented will concern those products.

In order to orient properly new materials in the field of textile finishing, it is necessary to make some

[1] Presented at the Sixth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., October 3, 1957.

comparisons. Therefore these reactants, in some cases, will be contrasted to the various urea derivatives and finishing resins with which they were paralleled in processing.

A comparison of the general properties of acetal reactants and two widely used urea derivatives can be seen in Table I.

Effects on Physical Properties

An important textile finishing property of the acetal reactants lies in the fact that they are a group of materials which cannot pick up chlorine. There is no nitrogen present in the molecule. The cellulose cross-links formed by the products may possibly contain acetalized polyhydric alcohols—certainly no place to retain chlorine.

It may also be said that the dimethylol ethylene urea products exhibit the property of being non-chlorine retentive—on freshly finished fabric. This, however, is a fleeting condition. After five or six commercial launderings (AATCC Method 14-53) some fabrics treated with the ethylene urea products actually display more severe tensile losses from chlorine damage than fabrics treated with ordinary urea formaldehydes which are expected to be chlorine retentive. In some such cases tensile losses amount to more than 80%.

It is this property of being unable to retain chlorine that constitutes one of the main advantages of the acetal reactants in the textile finishing field.

The range of crease resistance obtainable runs from low to high in the following order: glycol acetal, modified glycol acetal, urea formaldehyde, dimethylol ethylene urea, and pentaerythritol acetal.

Tensile losses should be considered in the same breath with crease resistance, for it is frequently stated that the two increase hand in hand. Such is not always the case. Among the acetal reactants the modified glycol acetal, which imparts medium crease resistance, gives almost no tensile loss. This fact makes it useful where some crease resistance is required but a shipping specification for the fabric allows for very little tensile reduction.

Durability of finish effects is an outstanding characteristic obtainable through the use of the acetal reactants. The word permanent is strong language in textile finishing, but these acetal reactants are so resistant to hydrolysis that it may be said that when they are gone—the fabric is gone, too!

A variety of hand effects may be obtained through the use of the acetal reactants. Treatment with the glycol acetal leaves the fabric actually softened. The pentaerythritol acetal imparts a hand somewhat like the dimethylol ethylene urea; i.e., very lively and springy with only a slight increase in fullness. The modified glycol acetal gives unusual fullness of hand.

The odors of the materials range from none to very strong. The glycol acetal has no odor of its own and develops none in processing. The modified glycol acetal has only a mild formaldehyde odor. In processing, only pentaerythritol acetal has a noticeably strong odor. The latter is removed from the fabric by the curing and afterwashing procedures.

Loss of abrasion resistance has always been very high on fabrics treated with resins. This factor has been especially favorable to both of the glycol acetal reactants listed here. By use of the AATCC Accelerotor on mill treated fabric, this laboratory has found the reduction of abrasion resistance to be almost nil. Other laboratories, using the Stoll machine, have reported occasionally that abrasion resistance actually has been increased by the treatment. There are, as yet, no data on the abrasion resistance of the pentaerythritol acetals.

It is generally recognized that finishing cotton fabrics with thermosetting and thermoreactive compounds reduces their absorbency. Treatment with the glycol acetal reactants makes a slight increase or no change at all in the absorptive capacity of a fabric. A mill laboratory, independently investigating this property, has reported that a bleached prepared cotton fabric displayed 198% moisture take-up before treatment with the glycol acetal and 192% afterward. Wet-out speed was the same before and after treatment.

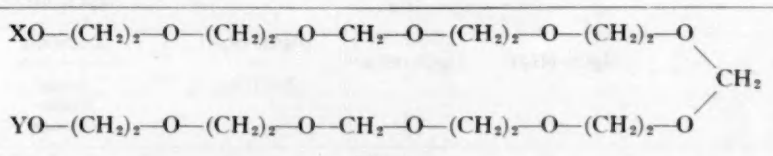

Fig. 1.

(X and Y are selected from a group consisting of H and CH_2OH; U. S. Patent 2,786,081.)

The glycol acetals produce no yellowing effects on cotton fabrics. The pentaerythritol acetal has shown some tendency to cause yellowing in laboratory ovens, where yellowing frequently occurs. There is no mill work on it with cotton. However, some rayon fabrics have been processed satisfactorily with no discoloration.

The cost of finishing with the acetals is of the same order as that of finishing with other thermoreactive and thermosetting materials. It is not usual for a fabric to be finished in a certain manner just for the purpose of obtaining a single enhanced property. There is nearly always a desire to obtain a combination of several enhanced properties, some of which are of more importance than others.

Table II is a check-off chart for the properties specifically requested on the ten mill treated fabrics for which evaluation data will be shown. The properties of non-chlorine retentiveness and dead set shrinkage control are most in demand. Hand, combining the requests for "very soft" with those for "permanently stiff," has been the next most im-

TABLE I. Properties of Acetal Treated Cotton Fabrics

		Acetal reactants			Urea derivatives	
		Glycol acetal	Modified glycol acetal	Penta-erythritol acetal	Dimethylol ethylene urea	Urea formaldehyde
Crease resistance on 80 × 80 fabric with untreated (W + F) value of 150°		Low 180°–210°	Medium 220°–235°	Very high 250°–300°	High 240°–280°	Medium high 240°–260°
Chlorine retention damage	Initial	None	None	None	Very low	High
	After several 212° F. launderings	None	None	None	Very high	High
Tensile loss		Medium 15–25%	Very low 0–15%	High 20–50%	Medium 15–25%	Medium 15–25%
Durability of effects		Permanent	Almost permanent	Permanent	Semi-permanent	Fleeting
Hand (without modifiers)		Very soft	Full; crisp	Soft; lively	Slight fullness; springy	Full; bouncy
Odor of product		None	Mild formaldehyde	Strong aldehyde	Medium formaldehyde	Strong formaldehyde
Retention of abrasion resistance		Excellent	Excellent	—	Poor	Bad
Absorbency		Slightly increased	No change	—	Decreased	Decreased
Effect on whites		None	None	Some yellowing	Faint yellowing	Slight yellowing
Catalysts		$MgCl_2 \cdot 6H_2O$	$MgCl_2 \cdot 6H_2O$	$MgCl_2 \cdot 6H_2O$ or $Zn(NO_3)_2$	$MgCl_2 \cdot 6H_2O$ $Zn(NO_3)_2$ Amine hydro-chloride	$MgCl_2 \cdot 6H_2O$ $Zn(NO_3)_2$ Amine hydro-chloride
Afterwash		Not necessary	Optional	Necessary	Generally recommended	Generally recommended

portant factor. Others, such as absolute freedom from odor and retention of absorbency, have not been requested as frequently, but they have been very important factors in the choice of a finish for the fabric whereon they have been requested.

The data in most of the following tables were obtained in mill laboratories. In some instances the fabrics were sent to these laboratories to be tested after completion of mill finishing.

Glycol Acetal—Gingham

The first fabric to be considered is a gingham. Table II indicates that permanent shrinkage control was a primary request for this fabric. The shrinkage control to be considered, however, was that of filling shrinkage. The gingham in question was fabric which had to be shipped to carry a "Sanforized" label. The shipping specifications called for a washed width of 35 in. Resin treatment, which could have helped to meet the shipping width specification, would have imparted chlorine retentiveness to the fabric and also would have eventually washed away sufficiently to allow considerable filling shrinkage to occur.

The regular finish for this type of fabric consisted of padding through a bath containing a starch ether and a softener, drying, and applying the "Sanforized" process. A glycol acetal and catalyst were added to the treatment bath and the fabric was cured 50 sec. at 310° F. A comparison of the data for the two finishes can be seen in Table III.

On the starch ether, softener finished fabric, the width shrank on the first laundering and continued shrinking through the tenth laundering, whereas the fabric treated with the glycol acetal showed only slight relaxation shrinkage in width on the first wash and did not change after that.

TABLE II. Specific Properties Requested on Fabrics

Properties requested	Glycol acetal						Modified glycol acetal			Penta-erythritol acetal
Primary emphasis * Also wanted x	Gingham	Sport denim	Sheeting	8-oz. Twill	Broadcloth	Knit goods	Broadcloth	Broadcloth	80×80 Print	Rayon dress goods
Dead set shrinkage control	•	•	•	•	x	•	x	x	x	•
Absence of chlorine retention	•		•		•	x	•	•	•	•
Odorless fabric	x	•	x	x	x	•	•	x	x	x
Odorless process						•				
Soft hand			•		•	•				•
Full hand							•	•	•	
Permanent stiff hand		•		•						
Retention of absorbency						•				
Low crease resistance					•					
Medium crease resistance							•	•	•	
High crease resistance										•
Increased yardage	•	•		•						

Glycol Acetal—Denim

A sport denim fabric presented an interesting combination of requested properties: (1) dead set shrinkage control, (2) a permanently built hand, (3) guaranteed absence of odor without afterwashing, and (4) a saving of yardage. The fabric was processed with a straight glycol acetal and a starch ether. The choice of the glycol acetal as the control agent eliminated any possibility of odor either in finishing or on finished fabric. The combination of the glycol acetal and the starch ether was used to impart the permanent firm bulky hand. The fabric was padded, can dried, cured 1 min. at 350° F., and treated with the "Sanforized" process.

Table IV presents a comparison of the data for the untreated sport denim, fabric treated with a modified ethylene urea product plus starch ether, and fabric treated with the glycol acetal and starch ether. Shrinkage measurements on the denim were carried out to 25 launderings for the purpose of thoroughly evaluating the durability of the dimensional control. The fabric with the glycol acetal treatment displays a small relaxation stretch on the first laundering and then holds to only 0.8% total shrinkage in the 25 laundering series. The untreated fabric shrinks immediately. The resin finished fabric shows characteristic creeping shrinkage on continued laundering.

TABLE III. Gingham

Formula
6.0% Glycol acetal
2.5% $MgCl_2 \cdot 6H_2O$
1.0% Starch ether
2.0% Softener

Processing
Padded
Can and frame dried
Cured 50 sec. at 310° F.
Sanforizer compressed

		Starch softener finish	Starch softener finish plus glycol acetal
Tensile strength, lb.	Warp	46	38
	Fill	33	31
Tear strength, lb.	Warp	3.6	2.9
	Fill	2.5	2.4
Width, in.	As finished	35½	35⅜
	After 1 212° F. laundering	33½	35¼
	After 10 212° F. launderings	33	35¼

The shrinkage evaluations are confirmed by the pick counts listed in the yardage output evaluation. On fabric starting with a greige pick count of 42, starch finishing and use of the Sanforized process to eliminate shrinkage would have required the manufacturer to take a 15% reduction in yardage. The line marked Sanforized represents the pick counts of fabrics as they would be finished for shipment. In both cases the fabrics with control agents are ready for delivery at 44 picks. Either of these finishing treatments will permit the manufacturer to ship this fabric at only a 5% reduction from the greige length, thus amounting to approximately a 10% increased output of fabric.

The row marked "After 25 launderings at 212° F." gives a picture of what can be expected by the purchaser and user of these fabrics. The glycol acetal treated cloth retains the dimensions at which it was sold; the resin treated cloth displays enough shrinkage that a garment made from it will cease to fit properly after several launderings.

The durability of these finishes was measured by means other than dimensional control. The fabric was carefully examined for weight retention. Rectangles of fabrics, each of which contained the same number of warp and filling yarns, were weighed before and after the series of launderings. There was little warp size to be washed out of the greige fabric. This can be seen in the weight drop from 3.8 to 3.5 g. Assuming the base weight of that area of cotton alone to be 3.5 g., the fabric treated with the modified ethylene urea lost $\frac{7}{12}$ of its added finish and the fabric treated with the glycol acetal lost $\frac{1}{11}$ of the added finish.

Another means of measuring finish durability is shown in the group of figures headed "Hand retention." These, however, were carried out under much milder laundry conditions. The Handlometer is an instrument which enables rapid determination of stiffness. In the use of that machine higher readings mean higher stiffness. The untreated fabric, in 25 launderings, lost warp stiffness, probably from loss of warp size. The two controlled fabrics gained stiffness, probably because washing removes the Sanforizing oils present and thus eliminates their slight softening effects.

On sport denim the glycol acetal finish gives the manufacturer the characteristics of shrinkage, hand, extra output of yardage, and freedom from odor on storage. At the same time it offers him the opportunity to deliver a better fabric to the eventual user.

TABLE IV. Sport Denim

Formula
6.0% Glycol acetal
6.0% $MgCl_2 \cdot 6H_2O$
6.0% Starch ether
1.0% Wetting agent
2.0% Sanforizing oil

Processing
Padded and can dried
Cured 60 sec. at 350° F.
Sanforizer compressed

		Untreated	Treated with modified ethylene urea product	Treated with glycol acetal
Yardage saved as illustrated by pick counts	Before "Sanforized" process	42	42	42
	After "Sanforized" process	49	44	44
	After 25 launderings at 212° F.	49½	47	44½
Percent shrinkage on laundering at 212° F.	1 Wash	14.6	1.3	1.0
	5 Washes	15.0	4.0	0.2
	15 Washes	15.5	6.2	0.8
	25 Washes	15.2	6.6	0.8
Percent progressive shrinkage		0.6	5.3	1.8
Finish retentions: weights of squares containing equal picks and ends, g.	As finished	3.8	4.7	4.6
	After 25 launderings	3.5	4.0	4.5
Hand retention: Handlometer measurements	Original	26 × 9	93 × 14	63 × 15
	After 25 140° F. launderings	14 × 10	97 × 28	76 × 22

Glycol Acetal—Sheeting

The sheeting described in Table V offers another demonstration of the high durability of the shrinkage control obtained through the use of the glycol acetal. The 3.8 × 3.0% shrinkage after 20 commercial launderings would not be a serious problem on an ordinary bed sheet. On a contour sheet, however, it is enough to force an inconvenient seam-straining stretch each time the sheet is put on the bed. At a minor expense of tensile strength and at no loss of tear strength, this fabric can be delivered as a dimensionally controlled fabric. Absolute freedom from chlorine retention is a necessity in a sheeting fabric. There can be no such thing as a sheeting fabric with low chlorine retention, because the laundering methods frequently used on sheets include strong bleaching procedures.

Glycol Acetal—Twill

An 8-oz. twill fabric presents another use for the combined properties of rigid shrinkage control and extra fabric yield. In this case the shrinkage control requirements are very rigid, because the fabric is to be subjected to the most severe laundering conditions. The glycol acetal finish meets the requirements, as shown by the data in Table VI.

The twill with the uncontrolled finish requires a Sanforizing compression of 8.6% to be delivered as a fabric controlled at the first laundering. Subsequent to the first laundering, this twill shrinks progressively up to the twentieth laundering and probably beyond that.

The same finish bath with glycol acetal added yielded fabric which required only 5.3% Sanforizer compression, thus allowing for 3.3% extra fabric

yield. This treated fabric shrinks less than 2% in a long series of launderings. It obviously ceases its minor progressing somewhere short of 15 launderings. This is accomplished at an expense of less than 15% of the original tensile strength. The initial tear strengths are considered acceptable, and after 20 launderings they are of the same order of magnitude as those of the uncontrolled finish. The increased cloth yield here covers the cost of the shrinkage control chemicals.

TABLE V. Type 128 Sheeting

Formula
6.0% Glycol acetal
6.0% $MgCl_2 \cdot 6H_2O$
1.0% Softener
1.0% Starch

Processing
Padded and can dried
Cured at 330° F.
Calendered
Sanforizer compressed

		Starch finish, excess Sanforizer compression	Glycol acetal finish
Tensile strength, lb.	Warp	67	66
	Fill	70	63
Tear strength, lb.	Warp	2.2	2.1
	Fill	3.0	3.0
Percent shrinkage after 20 launderings at 212° F.	Warp	3.8	0.1
	Fill	3.0	0.1

Glycol Acetal—Broadcloth

An extremely soft drapy hand with a suedy surface is obtained on one 144 × 68 broadcloth when finished for non-chlorine retentive dimensional control. This fabric was padded with the bath shown in the upper left hand corner of Table VII. It was then dried, cured 90 sec. at 320° F., and "Sanforized" processed 1 in./yd. The tensile loss accompanying this treatment is about 15%. Chlorine damage test values are shown here in pounds and indicate the expected absence of chlorine damage. The low order of crease resistance to be expected from treatments with the glycol acetal shows up here.

The tear strength measurements on this broadcloth are worthy of a comment aside from the main subject. The definite increase in tear strength

TABLE VI. Eight-Ounce Twill

Formula
8.0% Glycol acetal
3.0% Vinyl acetate
4.0% $MgCl_2 \cdot 6H_2O$
2.0% Softener
0.5% Wetting agent

Processing
Padded
Dried on a clip tenter
Cured 60 sec. at 350° F.
Sanforizer compressed

		Uncontrolled finish: Vinyl acetate emulsion plus softener	Controlled finish: Vinyl acetate emulsion plus softener with glycol acetal added
Fabric yield, %	Removed at Sanforizer	8.6	5 3
	Saved	—	3 3
Physical strength, lb.	Tensile strength	206 × 93	170 × 80
	Tear strength	10.0 × 7.0	6.9 × 5.4
	Tear strength after 20 launderings at 212° F.	7.1 × 7.3	6.9 × 5.8
Percent shrinkage in successive 1-hr. launderings at 212° F.	1 Wash	8.6 × +1.7	+0.3 × +0.8
	15 Washes	11.9 × +0.3	1.4 × +0.3
	20 Washes	12.2 × −0.3	1.4 × +0.3
	Progression	3.6 × 2.0	1.7 × 0.5

shown in the last line was confirmed by two laboratories. It is to be attributed to the polyethylene softener used in the processing bath. The natural softness of the glycol acetal finish may have made it easier for the polyethylene softener to produce this effect.

Glycol Acetal—Cotton Knit Goods

The dimensional control of cotton knit goods is a matter of reducing shrinkage to an acceptable level. With proper mechanical handling, several types of resins and dimensional control products will do this. Absence of chlorine retention and freedom from odor are also properties to be desired in the finishing of certain cotton knit goods; these two requirements eliminate many products. Retention of the original absorbency of the clean bleached cotton is still another very desirable property in a cotton knit garment. All four properties have been obtained on the knit goods, for which the evaluation data are shown

TABLE VII. 144 × 68 Broadcloth

Formula

8.0% Glycol acetal
2.5% $MgCl_2 \cdot 6H_2O$
2.0% Softener
0.1% Wetting agent

Processing

Padded
Tenter dried
Cooled and batched
Cured 90 sec. at 320° F.
Sanforizer compressed 1 in./yd.

		Untreated	Glycol acetal treated
Percent shrinkage in successive 1-hr. launderings at 212° F.	1 Wash	3.7 × 3.1	0.0 × 0.5
	5 Washes	4.3 × 3.4	0.4 × 0.5
	10 Washes	4.5 × 3.2	0.7 × 0.6
Chlorine damage	Control	114	98
	Chlorine treated	114	94
Tensile values, lb. (AATCC 69–52)	Chlorine treated after 5 washes	109	98
Crease resistance (W + F)	As finished	166°	206°
	After 5 washes at 212° F.	171°	195°
Physical strength, lb.	Tensile	114 × 56	98 × 45
	Tear	2.0 × 1.3	2.9 × 1.9

TABLE VIII. Cotton Knit Goods

Formula

8.0% Glycol acetal
8.0% $MgCl_2 \cdot 6H_2O$
1.0% Softener

Processing

Impregnated at 70% wt./vol.
Spread (wet) to greige width
Dried at 250° F.
Cured 20 min. at 250° F.
Steam calendered to 1 in. less than greige width

			Uncontrolled finish	Same finish plus glycol acetal
Shrinkages, %	1 Wash	Width	13.5	6.3
		Length	7.2	4.0
		Total	20.7	10.3
	5 Washes	Width	10.5	5.0
		Length	9.2	5.2
		Total	19.7	10.2
Ball burst strength, lb.			82	62
Odor			None	None
Chlorine retention			None	None

TABLE IX. 144 × 60 Broadcloth

Formula

8.0% Modified glycol acetal
6.0% Magnesium chloride catalyst
2.0% Polyethylene softener
1.0% Wetting agent

Processing

Padded
Frame dried
Batched (cool)
Cured 90 sec. at 340° F.
Calendered

(No untreated fabric available for testing)		As finished	After 5 commercial launderings
Warp tensile strength, lb.		85	—
Warp tear strength, lb.		2.4	—
Chlorine retention (AATCC 69–52)	Original	85	84
	After Cl_2 treatment	84	85
	Loss %	1	0
Warp shrinkage, %		0.2	0.9
Crease resistance (W + F)		224°	204°
Hand		Full	Full

in Table VIII. The shrinkage has been reduced to an acceptable level, and the effect, produced with no reduction in absorbency, is obviously durable. The absorption capacity of the fabric was approximately 300% both before and after treatment.

Modified Glycol Acetal—Broadcloth

Table IX presents a 144 × 60 broadcloth finished with the modified glycol acetal. A very full hand coupled with medium crease resistance and no chlorine damage are the results of finishing with this product. Note, in the column on the right, that a series of 212° F. launderings does not alter the non-chlorine retentiveness of this finish.

Modified Glycol—Cotton Prints

On a printed 80 × 80 cotton a very full hand, medium crease resistance, no odor, and minimum chlorine retention were the finishing objectives. The fabric was padded in the bath for which the formula is shown in Table X. The results obtained by the use of the modified glycol are compared to those obtained by the use of a modified melamine resin finish.

The chlorine damage figures are interesting in the fact that the untreated fabric displays susceptibility to chlorine attack. The weakening of the fabric occurs in the printed areas, and is undoubtedly caused by materials used in the printing. The fabric treated with the modified glycol acetal displays no

TABLE XI. 80 × 80 Print Cloth

		Untreated	Treated
Tensile strength, lb.	Warp	65	53
	Fill	46	39
Tear strength, lb.	Ward	2.5	1.9
	Fill	1.4	1.2
Crease resistance (W + F)		151°	229°
Warp tensile strength (chlorine treated)		63	52
Percent chlorine damage		3	2
Percent shrinkage on launderings at 212° F.	1 Wash	4.0 × 0.3	1.0 × 0.8
	5 Washes	4.8 × 0.5	1.4 × 0.8

TABLE X. 80 × 80 Cotton Prints

Formula

6.0% Modified glycol acetal
1.4% Durable water repellent
2.7% Magnesium chloride catalyst
0.8% Polyethylene softener

Processing

Padded
Frame dried
Cured 85 sec. at 345° F.
Sanforizer compressed

		Unfinished	Finished with modified glycol acetal	Finished with modified melamine resin
Percent tensile loss from chlorine damage	As finished	27	27	61
	After 5 washes at 212° F.	28	27	82
Odor		None	None	Detectable formaldehyde
Crease resistance (W + F)	As finished	158°	228°	221°
	After 5 washes at 212° F.	176°	208°	188°
Tear strength, lb.	As finished	2.7 × 1.5	2.2 × 1.2	2.2 × 1.2
	After 5 washes at 212° F.	2.2 × 1.6	2.4 × 1.3	2.0 × 1.2
Tensile strength, lb.		72 × 43	59 × 34	54 × 36

additional chlorine retention damage either originally or after several boiling washes. This is in contrast to the modified melamine resin finish, which shows extra chlorine damage on the finished fabric and permits further increase with subsequent launderings.

The effects on tensile and tear strength are about the same with both finishes, but the crease resistance obtained with the modified glycol acetal is slightly higher to begin with and is decidedly more durable. These treated goods were examined for odor by placing samples in a jar with small amounts of moisture. The jars were held 16 hr. at 120° F. and opened for odor inspection. The acetal finished fabric gave off no odor.

Table XI, concerning another 80 × 80 print cloth, presents another example of medium crease resistance and no chlorine damage to fabric treated with the modified glycol acetal.

Pentaerythritol Acetal

Up to the present time there has been no mill work done on cotton with the pentaerythritol acetal. A relatively high cost, a tendency to yellow, and tensile losses of the order of 50% have caused this product to be withheld from cotton processing. A cleaner raw material at a somewhat lower price has been helpful in alleviating the first two problems; an investigation into methods of catalysis shows some promise of helping reduce the high tensile losses. At this point cotton processing may become perfectly feasible. It will be necessary to use laboratory data for the effect of the pentaerythritol acetal on cotton and to reach into rayon processing for mill data to give some idea of the performance of the product in mill finishes.

Table XII gives the evaluation data on some printed rayon dress goods. The crease resistances obtained are high and stay high after very severe launderings. The shrinkage control, for a rayon fabric, is excellent. A nonnitrogenous product such as this would not be expected to show chlorine damage and such is the case—it does not. Tensile losses from this treatment amount to about 20% in each direction. Laboratory work on cotton with the pentaerythritol acetal has led to durable crease resistance as high as 300° (W + F). However, treatments which do this have (in laboratory processing) produced drastic tensile losses—of the order of 50% of the fabric strength. Data for the laboratory processed fabric evaluated and presented in Table XIII show the effect of treating to obtain medium high crease resistance. Note that the tensile loss at this level is about 37%. The crease resistance shows

TABLE XII. Rayon Dress Print

Formula

30.0% Pentaerythritol acetal
1.5% Oxalic acid
1.5% Softener

Processing

Padded
Dried at 260° F.
Cured 2 min. at 360° F.
Afterwashed (slack)
Extracted
Loop dried
Steam framed
Semidecated

		Untreated	Treated
Crease resistance	As finished	177°	294°
	After 10 212° F. washes	237°	280°
Shrinkage, %	Original	12.0 × +2.9	1.1 × +0.4
	After 10 212° F. washes	13.6 × +1.8	2.1 × 0.2
Tensile strength, lb.		60 × 62	48 × 48
Tear strength, lb.		1.4 × 2.6	2.1 × 2.7
Chlorine damage		None	None

TABLE XIII. 108 × 58 Broadcloth — Lab Processed

Formula

20.0% Pentaerythritol acetal
6.0% $MgCl_2 \cdot 6H_2O$
1.0% Softener

Laboratory Processing

Padded at 100% wt./vol.
Framed to original dimensions
Dried at 180° F.
Cured 90 sec. at 315° F.
Afterwashed
Dried at original dimensions

		Water blank	Treated
Crease resistance (W + F)	Original	150°	247°
	After 5 washes	193°	241°
Percent shrinkage in laundering at 212° F.	Original	5.3 × +3.5	1.7 × +1.3
	After 5 washes	6.7 × +3.4	1.9 × +1.5
Tensile strength, lb.		84 × 37	53 × 22
Tear strength, lb.		1.7 × 1.1	1.6 × 0.6

exceptional durability, and, of course, chlorine damage cannot occur.

Summary

In conclusion, the unmodified glycol acetals, one of which is commercially available as Quaker Reactant SC, offer themselves as odorless, non-chlorine retentive materials which can be used to impart permanent dimensional control with a completely soft hand with no reduction in absorbency, or a permanently built hand when used with starch ethers. In both cases the major portion of the abrasion resistance of the original fabric will be retained. The soft hand fabrics suggest knit goods and other fabrics where retention of absorbency is very important. The built hand fabrics suggest denims, interlinings, buckrams, and other stiffened fabrics. Other applications will undoubtedly suggest themselves as the use of this type of finishing chemical expands.

The modified glycol acetals, one of which is commercially available as Quaker Reactant 16, present non-chlorine retentive dimensional control agents which may be used to impart a bulky hand when only medium crease resistance is required, hold a starch ether hand, add bulk to higher crease resistance finishes without detracting from the crease resistance and without adding any odor or chlorine retention, and protect tensile strength in finishing. Other uses will also become part of the performance pattern of these materials.

For the acetals of the pentaerythritol type there is at present not enough mill process information to be positive what specific textile finishing position they will eventually occupy. However, they have been planned and developed for the purpose of imparting durable high crease resistance to white cotton fabrics. The fabrics so produced can be completely free from chlorine retention. Recent industry-wide efforts to produce such fabrics have led to a considerable amount of research and discussion and to some rather expensive and involved finishing procedures. It is expected that the pentaerythritol acetals, one of which is Quaker Reactant X-1582, will be materials which will accomplish this end at a reasonable cost and by the usual finishing operations.

Acknowledgments

The authors wish to express their appreciation to Mr. T. J. Cronin and Mr. J. H. Davids, who carried out some of the application and testing work involved in this study.

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The Reactivity of Cellulose[1]

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Abstract

The chemical finishing of cotton involves applying to it materials that either react with the cellulose or with one another after they have been adsorbed by the cellulose. For finishes of the first kind it is obviously important to have the cellulose in a reactive condition, but it is no less important for the second kind also, since reactivity and accessibility are in general closely correlated.

This paper discusses the reasons underlying the great differences of reactivity that can be encountered among samples of cellulose that appear to be identical chemically and differ only in physical form or structure. Moisture absorption studies exemplify these differences and build a theory that goes far to explain them in terms of variability of the availability of the reacting groups in the cellulose molecule. Thus purified cotton is in general in a state of low reactivity and regenerated cellulose in one of high reactivity, while mercerized cotton occupies an intermediate position. This picture is for most reactions satisfactory, but in some it is completely reversed, with ordinary cotton having a high reactivity and regenerated cellulose a low, mercerized cotton being again intermediate. The cause of this is discussed in the light of more recent work.

THE word "reactivity" when applied to cellulose refers to the rate at which cellulose in its various forms reacts, and hence is a concept in the domain of physical chemistry. Yet if one consults the indexes of the standard textbooks of physical chemistry one finds virtually no reference to it. The reason for this reticence is that comparatively little is known about the kinetics of heterogeneous reactions; the appropriate parts of the textbooks usually say a little about particle size and a very great deal about heterogeneous catalysis, but nothing at all on the lines of the treatment accorded to the kinetics of homogeneous reactions. One can well understand the reluctance of those who are able to choose their research topics to start work on such a difficult and possibly unrewarding subject, but those who are concerned with cellulose and its reactions cannot escape the necessity of considering it. It is because of the lack of solid fundamental background that so much of this discussion will be qualitative rather than quantitative, and vague rather than precise.

Even when attention is limited to the heterogeneous reactions in which cellulose is involved, the field is still much too large for adequate discussion here; there are several topics within the ambit of the title that will be dismissed with their mere mention. There is plenty of evidence that the effect of chain length on reactivity is either completely negligible or so small that it need not concern us further. On the question of the relative rates of reaction of the different hydroxyl groups in the cellulose molecule, much work has been done, particularly on this side of the Atlantic, by Purves [1], Malm [2], and their collaborators, but from our present point of view these differences are of second order. Again, modification of the cellulose molecule occurs very readily at the hydroxyl groups, so that substitution at these groups generally reduces the susceptibility to attack; this also will not be considered further.

The purpose of this paper is to discuss the reasons underlying the great differences in reactivity of samples of cellulose that appear to be identical chemically and differ only in physical form or structure.

Figure 1 [3] relates the amount of water taken up by a purified cotton to the relative vapor pressure, or relative humidity, of the atmosphere to which it is exposed. The lower of the two curves was obtained by adding water to dry cotton, and the upper by removing it from cotton that had been

[1] This paper was presented at the Sixth Chemical Finishing Conference of the National Cotton Council of America, Washington, D. C., October 2, 1957, and at the joint meeting of the Fiber Society and the Textile Institute, Boston, Mass., September 5, 1957.

allowed to come to equilibrium with a saturated atmosphere. The two curves are quite distinct, and the two values corresponding to any given vapor pressure do not approach one another more closely if the samples are left in the same atmosphere for a long time. They represent, in fact, true though different equilibria.

It is clear, therefore, that the amount of water sorbed is not determined uniquely by the vapor pressure and temperature, but depends also on the previous history of the sample. Moreover, later work showed that these two curves are to be taken not as the locus of all possible equilibrium conditions, but as defining an equilibrium area, any point in which can represent the amount of contained water under suitable conditions of pressure and prehistory. This is illustrated by the curves shown in Figure 2, from which it is evident that more limited cycles do in fact follow intermediate paths.

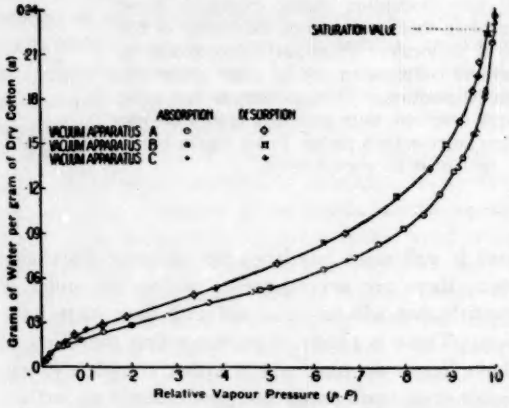


Fig. 1. Absorption and desorption by soda-boiled cotton at 25° C.

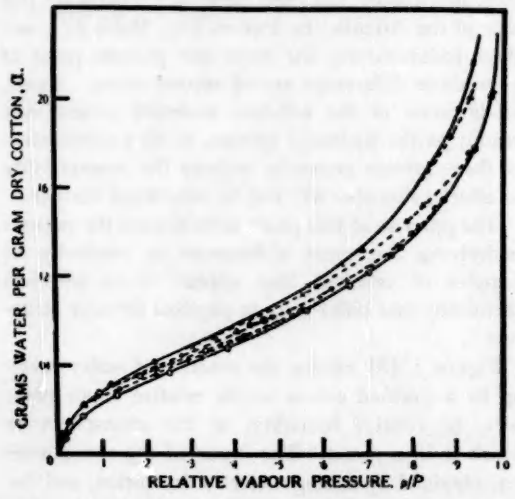


Fig. 2. Water sorbed versus relative vapor pressure.

This phenomenon of hysteresis is of course well known now, and in considering an explanation of it we need not enlarge on the usual picture of cellulose as consisting of both crystalline and amorphous regions, with gradual transitions from one to the other, and with molecules so long in comparison with the length of the crystallites that one molecule may extend through more than one crystalline and more than one intermediate amorphous region. It is also agreed that the hydroxyl groups of the cellulose molecules constitute the places where the bulk of the water is held by hydrogen bonding, and that this will occur partly on the crystallite surfaces but mainly in the amorphous regions of the structure.

When cellulose is formed within the cotton fiber it is in the presence of water, and the hydroxyl groups whose residual combining power is not satisfied by combining with one another in the crystallites will have water molecules attached. As the fiber dries, some of these groups will be freed, and it is reasonable to assume that the cellulose molecules will tend to rearrange themselves so that where possible these free hydroxyl groups may bond to one another. If the cotton is dried over a desiccant at room temperature this process will go on until all the attached water has been removed, although it will proceed with increasing difficulty as relative movement of the molecules is hindered by the links already formed. But though there is a tendency for this rearrangement to occur, it may not always occur; some molecules will be held together more closely than others, and it may be that a change of configuration is possible only when a loosely bound molecule attains momentarily a sufficiently large amplitude of vibration. When this explanation was first put forward it was considered that even completely dry cellulose might contain some free hydroxyl groups, but recent infrared work [4] has indicated that the number of free hydroxyl groups can only be small under any conditions. However, this requires a slight modification rather than a serious alteration of the picture, since that work has itself shown that in the amorphous regions the strength of the hydrogen bonds is variable.

If dry cellulose is now allowed to absorb water, the absorption will occur in the first instance on any free groups that remain, or on those groups held together with hydrogen bonds of lowest strength, but the number of groups available for absorption will increase as absorption proceeds, since a proportion of those momentarily freed by thermal vibration will be prevented from recombining by the speedy attachment to them of water molecules. The number of positions available during absorption will tend to be less than during desorption, because the amplitude of vibration of a molecule held to another by the attraction of one or more active groups will be less than that of a molecule in which the active groups are free.

This explanation of hysteresis therefore postulates that during desorption and absorption the number of hydroxyl groups available for the attachment of water decreases and increases respectively, but with a lag during absorption, so that for the same number of active groups the humidity will be greater during absorption than during desorption.

This is only one possible explanation of hysteresis, but it is one that is particularly interesting in the present context. Most of the reactions of cellulose are those of its hydroxyl groups, and a study of moisture absorption is a convenient method of assessing their accessibility. From what has been said already it would be anticipated that reactions involving hydroxyl groups should proceed more readily if the cellulose is not completely dried out to make these groups less accessible, and there is in fact a fair amount of evidence in support of this, even in such mundane matters as the depth of shade assumed by cellulose fibers when dyed in a given dyebath.

The uptake of water is an exothermic reaction, and it follows as a thermodynamic necessity that the amount of water taken up at constant partial vapor pressure decreases with increasing temperature. This effect has been studied in some detail for cotton, and Figure 3 [5], which shows a series of isotherms for the sorption of water by cotton cellulose at temperatures in the range 10–50° C., provides experimental confirmation of the theoretical deduction. Figure 4 [5] shows that the same effect is evident in the range 50–100° C. at humidities below about 85%, but at higher humidities the curves cross one another, indicating that in this region the amount of water taken up at constant humidity *increases* with increasing temperature.

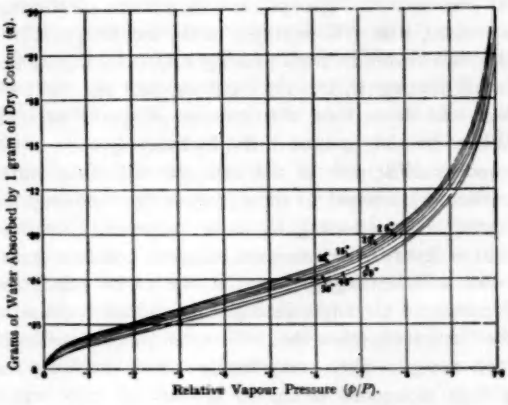


Fig. 3. Absorption of water by soda-boiled cotton at 10–50° C.

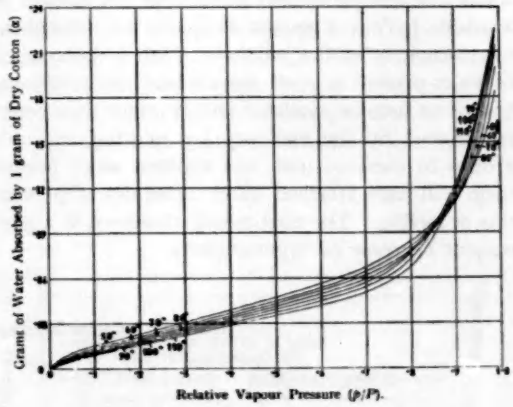


Fig. 4. Absorption of water by soda-boiled cotton, at 50–100° C.

Two additional experimental observations are of interest. It has been noted that drying out at room temperature causes a temporary reduction in the amount of water sorbed, and that this reduction is removed by exposing the sample to a saturated atmosphere, so producing the hysteresis effect. But if a sample of cotton is dried for some time at a high temperature (for example, 110° C.) its capacity for taking up water is more or less permanently reduced, both absorption and desorption curves being lower than the corresponding curves for unheated cotton [6]. On the other hand, if it is heated under suitable conditions in the presence of a high concentration of water vapor, its hygroscopicity may be increased [7]. The molecules of the cellulose, and in particu-

lar the hydroxyl groups, are in a state of thermal vibration that will increase with the temperature; this can result in both making and breaking of the bonds linking hydroxyls together, and the final effect will depend on the amount of water present. Where it is high, most of the hydroxyl groups in the noncrystalline part of the cellulose will have water molecules attached to them; hence the tendency for further cross-bonding to occur by mutual satisfaction of hydroxyl groups on adjacent cellulose molecules will be negligible. On the other hand, the breaking of already existing links, which because of the increased vibration will occur more readily at high temperatures, may easily result in both the groups concerned failing to recombine, since water molecules will probably attach themselves before recombination becomes possible. The final result is a more or less permanent increase in the number of available hydroxyl groups, hence in the subsequent hygroscopicity of the cellulose. But if the amount of water present is small, the tendency for additional groups to become available will be more than counterbalanced by the tendency for existing available groups to combine with one another, since few of them will have attached water molecules to prevent this occurring. The final result, therefore, is a permanent decrease of hygroscopicity.

Since heating in a saturated atmosphere increases the hygroscopicity of cotton, and heating in an atmosphere of low humidity decreases it, it is to be expected that at some point between the two extremes no alteration will be produced. The existence of such points is suggested by the intersections of the high-temperature isotherms, but it is more instructive to consider these from another point of view. The general effect of increasing the temperature is to decrease the moisture uptake of cotton in equilibrium with an atmosphere of constant relative humidity by decreasing the average amount sorbed per active group, as was shown by the curves for the temperature range 10–50° C., but if the temperature and amount taken up exceed certain values the resulting increase in the number of active groups may be sufficient to counterbalance the decrease in the average amount attached to each group, so that the temperature effect appears to reverse.

It will now be evident that the reactivity of cotton can be increased to some extent by treatment with water at high temperatures, and decreased by heating in the absence of water, but before examples of such treatments are given it is desirable to take one more step in following this study of moisture absorption, and in doing so to come to the most obvious connection between moisture absorption and reactivity.

TABLE I. Cotton Mercerized in 15% Sodium Hydroxide

Absorption				Desorption			
	α				α		
p/P	Mercerized	Soda-boiled	α Mercerized/α Soda-boiled	p/P	Mercerized	Soda-boiled	α Mercerized/α Soda-boiled
.05	.0207	.0141	1.47	.95	.2685	.1830	1.47
.10	.0300	.0198	1.52	.90	.2106	.1500	1.40
.15	.0372	.0246	1.51	.85	.1797	.1311	1.37
.20	.0441	.0282	1.56	.80	.1623	.1176	1.38
.25	.0507	.0321	1.58	.75	.1482	.1053	1.41
.30	.0582	.0366	1.59	.70	.1362	.0960	1.42
.35	.0654	.0405	1.62	.65	.1257	.0873	1.44
.40	.0723	.0447	1.62	.60	.1164	.0792	1.47
.45	.0792	.0492	1.61	.55	.1074	.0726	1.48
.50	.0870	.0537	1.62	.50	.0993	.0669	1.48
.55	.0945	.0582	1.62	.45	.0906	.0606	1.49
.60	.1023	.0630	1.62	.40	.0822	.0552	1.49
.65	.1110	.0690	1.61	.35	.0744	.0498	1.49
.70	.1206	.0756	1.60	.30	.0669	.0450	1.49
.75	.1308	.0831	1.57	.25	.0588	.0396	1.48
.80	.1446	.0939	1.54	.20	.0513	.0348	1.47
.85	.1620	.1056	1.53	.15	.0438	.0297	1.47
.90	.1875	.1230	1.52	.10	.0366	.0246	1.49
.95	.2349	.1515	1.55	.05	.0267	.0171	1.56
			Mean 1.57				Mean 1.46

The technical processes that are normally applied to textile fibers have in general a fairly small effect on their capacity for absorbing water; with cotton, for example, the differences caused by most processes are smaller than the uncertainties that can be ascribed to unknown differences of prehistory. There are, however, some important exceptions; in particular, processes that cause large swelling of the fiber result in large increases of hygroscopicity. Possibly the most important of these, and certainly that which has received most study from this point of view, is mercerization. This involves steeping cotton or other cellulose fiber in a solution of a caustic alkali, the concentration of which must exceed a minimum value determined by the fiber, the temperature, and the particular alkali used. An enormous lateral swelling of the fiber results, and usually the technical process is conducted in such a way that the accompanying longitudinal shrinkage is either prevented or allowed to occur and then counteracted by stretching, but the most pronounced swelling action is achieved when the fiber is free to change its dimensions without any external restraint.

Figure 5 [8] shows the isotherm for a sample of loose scoured cotton that had been immersed in a 15% solution of sodium hydroxide, washed, and dried. The isotherm for the original unmercerized cotton is also shown, and it is obvious that a large increase in hygroscopicity has resulted from the treatment. The general shape of the curves is, however, the same; in fact, the curves for the mercerized cotton can be obtained from those for the unmercerized by multiplying the ordinates of the latter by a factor that is pretty well independent of the humidity. This is shown in Table 1 [9], where it will be seen that the ratio of the moisture uptake of the mercerized cotton to that of the original scoured cotton is roughly constant. Almost certainly this is an approximation only—trends are in fact evident from the Table—and it may well be that, as suggested by at least one of the two-phase theories of adsorption, only the closely bound water should demonstrate the constant ratio, but for the present purpose the ratios of total water sorbed are sufficiently constant to

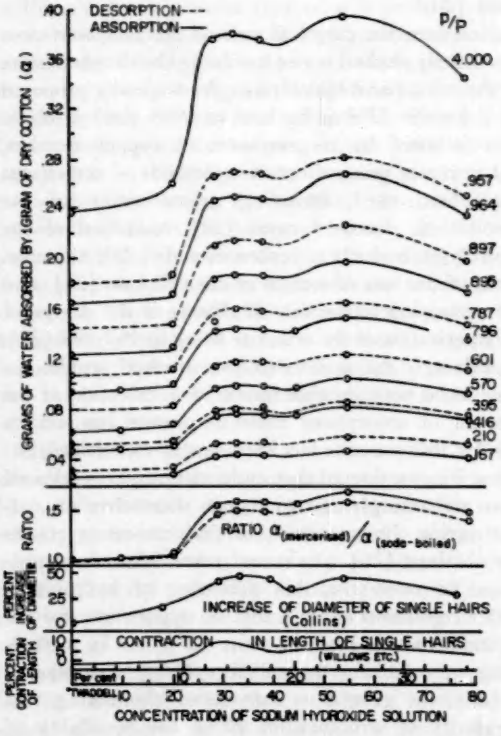


Fig. 5. Absorption and desorption of water by mercerized cottons at 25° C.

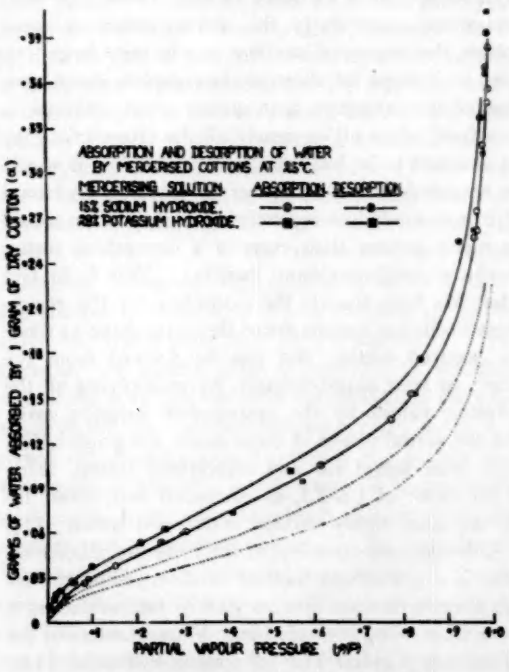

ABSORPTION AND DESORPTION OF WATER BY MERCERISED COTTONS AT 25°C.
MERCERISING SOLUTION. ABSORPTION. DESORPTION.
15% SODIUM HYDROXIDE.
28% POTASSIUM HYDROXIDE.
GRAMS OF WATER ABSORBED BY 1 GRAM OF DRY COTTON (α)
PARTIAL VAPOUR PRESSURE (p/p)

Fig. 6. Effect of concentration of sodium hydroxide solution.

justify the acceptance of their mean value as a measure of the change in the sorptive capacity of the cellulose brought about by the mercerization process.

The effect of the concentration of the mercerizing alkali is shown in Figure 6 [10], where the amounts sorbed at different values of the partial pressure are plotted against the concentration; it is seen that there are two maxima in the curves. In itself this is of no special interest for the present purpose, but when it is compared with the curves showing the swelling of the fiber in relation to concentration, we see that the sorption curves are similar in shape to the swelling curves. This was one of the earliest occasions on which the intimate relation between moisture uptake and swelling was demonstrated, and it is of particular interest because of the close relation between degree of swelling and general reactivity. It provides, in fact, yet another justification for the approach adopted.

In the very great opening up of the structure that occurs in mercerization, there is a large increase in the number of hydroxyl groups available for combining with water, dyes, etc. Naturally the degree of swelling and the water sorption go hand in hand, both being due to the same primary cause. In mercerization, particularly the mercerization of loose cotton, the degree of swelling can be very large, but even so it stops far short of the complete disintegration of the structure that occurs when cellulose is dissolved, when all or nearly all the cross-links may be assumed to be broken. Because of this, it would be expected that the number of available hydroxyl groups in a cellulose regenerated from solution would be much greater than even in a mercerized cotton produced with maximum swelling. This is in fact what has been found; the isotherms for the regenerated-cellulose rayons are of the same shape as those for scoured cotton, and can be derived from the latter, at least approximately, by multiplying all the sorption values by the appropriate sorption ratio. But the actual values of these ratios are greater than have been found for any mercerized cotton, being of the order of 1.8–2.1, as compared with about 1.6 for the most highly swollen mercerized cotton [11].

Although measurement of the moisture absorption ratio is a convenient method of determining the effect of an activation process such as mercerization, it is far from being the only one. Measurements of the absorption of iodine [12], of sodium hydroxide [13], and of barium hydroxide [14] from their dilute solutions have been used, as well as the absorption of copper from a dilute solution of cuprammonium hydroxide [15]. There is little to choose among these methods for assessing the probable behavior of cellulose in most of its reactions, which generally occur in the presence of liquid water, but the moisture absorption method is the only one so far considered that can be used to assess the condition of air-dry cellulose, where the swelling is less than in water. Chemical methods of measuring the increased reactivity of mercerized and regenerated celluloses have also been proposed. One early method developed at the Shirley Institute was to submit the sample to a standardized oxidation with sodium hypobromite and measure the copper number of the cellulose before and after oxidation [16]. Other oxidation methods that have been developed recently include oxidation with periodate [17] and with chromium trioxide [18]; the latter is claimed to give results in fair agreement with those obtained by the thallation technique developed by Purves [19] and his co-workers, which is rather complicated for everyday use. Deuterium exchange has also been used [20].

However, the chemical method that has been most intensively studied is one involving the determination of the rate of acid hydrolysis. As originally proposed by Schwalbe [21] as far back as 1908, the hydrolysis was followed by measurement of copper number, but in recent years alternative methods of assessment have been used, including determination of the amount of glucose formed [22], oxidation of the hydrolysis products to carbon dioxide [23], measurement of the loss of weight of the cellulose [24], and determination of the rate of change of the degree of polymerization of the cellulose being hydrolyzed [25].

Although the acid-hydrolysis method would appear to be very suitable for the determination of the amount of amorphous material present, in fact its use for this purpose has been severely criticized, because it is considered that molecular residues released from the amorphous regions can themselves crystallize during the treatment, so that erroneous results are obtained [26]. In recent years it has been proposed to overcome this difficulty by hydrolyzing under conditions so mild that no opportunity for recrystallization is likely to arise [27] and by methylating or oxidizing the cellulose before hydrolyzing it [28], the groups so introduced eliminating that regularity of structure on which the possibility of crystallizing depends.

The various methods that have been mentioned do

in fact present a logical and satisfactory picture of the state of cellulose in relation to its behavior towards aqueous solutions, its dyeing behavior, its hygroscopicity, and its general chemical reactivity. In this last respect ordinary cotton cellulose is the least reactive and regenerated cellulose the most reactive, with mercerized cotton occupying an intermediate position. The same kind of generalization can be made for wood celluloses, with some differences in detail.

Application of these ideas to some of the better known reactions to which cellulose is submitted is now considered. The first step in the making of viscose rayon is the making of alkali cellulose, and the normal way of doing this is to steep sheets of wood pulp in caustic soda solution and express the excess liquor. The concentration of the caustic soda solution is such that the cellulose is in fact mercerized, therefore in a highly reactive condition. However, an inevitable result is that the retention of liquor is high, and high pressures have to be used to reduce that retention to a desirably low value. In the old batch process that is still probably the normal one, the application of high pressures is not particularly difficult, but in the continuous processes that were developed originally in Germany it is much less easy. The difficulty was mitigated by increasing the temperature of the steeping liquor [29], which contributes in two ways—by making expression easier and by reducing the swelling. But reducing the swelling also reduces the reactivity, and there was a good deal of evidence that the quality of the rayon produced was lower than we are accustomed to expect. Not all of this reduction in quality is necessarily attributable to the increased steeping temperature, but the example is useful in showing how the possibility of activating cellulose is utilized in industrial processes.

Etherification is in many respects similar. Cellulose is usually treated with caustic soda solution to form soda cellulose before it is treated with the etherifying agent, and the solution used is above the minimum concentration necessary to mercerize the cellulose, for the reaction proceeds more rapidly and to a greater extent the greater the swelling of the cellulose in the preparatory treatment. In etherifying with diazomethane, a process in which the cellulose is not treated with alkali and hence is not activated, the degree of etherification achieved in a standardized process increases directly [30] with the moisture content of the cellulose being etherified.

A similar effect is familiar to all concerned with the commercial production of cellulose acetate. This involves treatment of cellulose with acetic anhydride, a catalyst, and a solvent for the cellulose acetate produced; adequate cooling must be provided to prevent the temperature rising too high, which would result in severe degradation. When this does happen with any particular batch, the first thing that the manufacturer checks is the moisture content of the cellulose prior to acetylation, particularly if it comes from a bleaching department that is paid a bonus on weight turned out. The reverse effect, though naturally much less common in these circumstances, is not unknown. If the cellulose is too dry, its rate of acetylation can be very low, so that between the extremes the moisture content must be controlled carefully to ensure the regular production of a satisfactory product. Moreover, the effect of local high-temperature baking is occasionally encountered, producing small tufts of fibers that are extremely resistant to acetylation.

It is seen that, compared with ordinary cotton, mercerized cotton has about 50% greater availability of hydroxyl groups, and regenerated cellulose about 100% greater. If now we apply an ordinary acetylation process to these three materials, instead of finding that the rate of acetylation increases more or less in conformity with expectation, we find that mercerized cotton acetylates very much more slowly than ordinary cotton, while regenerated cellulose cannot be acetylated at all in a reasonable time. There is in fact a complete reversal of the picture that has been presented. However, no very great change is needed to restore it. The reversal occurs when mercerized or regenerated cellulose is before acetylation allowed to become air dry by evaporation of the water—not necessarily at a high temperature. But if instead the excess water is removed by washing with acetic acid, and the cellulose containing the acid is acetylated, the different celluloses react in the expected order—regenerated cellulose the fastest and unmercerized cellulose the slowest. It is important to distinguish between this kind of activation and another variety generally known in the industry as "pretreatment." In industrial manufacture it is common to mix with the air-dry cellulose about a third of its weight of acetic acid before introducing it into the acetylation mixture; this speeds up the reaction appreciably, though it is not always used industrially because of the greater difficulty of controlling the

temperature in the faster reaction. But a treatment of this kind does not restore the expected order in the rates of acetylation of ordinary, mercerized, and regenerated celluloses; the order is restored only if the celluloses after activation are not even air-dried, and the excess water present is replaced with acetic acid or other suitable organic substance. This industrial pretreatment is probably related more to preserving the state of reactivity corresponding to the original moisture content, rather than deactivating it by immersing it in a dehydrating mixture containing acetic anhydride.

Although these effects have been known for a long time to those engaged in the production of cellulose acetate, it is only comparatively recently that an account of any study of them has appeared in the scientific literature, and that mainly by Staudinger [31] and his collaborators. There are two distinct effects to be explained: the reversal of the normal order when the air-dry celluloses are acetylated and the change brought about by replacing the water with acetic acid, pyridine, and the like. No soundly-based explanation of the reversal is yet available. Staudinger has suggested that ordinary cellulose acetylates more rapidly than mercerized because mercerizing, in addition to altering the structure of the cellulose, also removes impurities such as uronic acids, which in the unmercerized cotton prevent the cross-linking that slows down the reaction in the mercerized material. This explanation obviously is untenable, because the reversal effect is no less pronounced in celluloses from which all such impurities have already been removed. It seems much more likely that the effect is directly related to the amount or strength of cross-bonding that occurs in the different forms of cellulose. During mercerization the degree of swelling is so large that there is a large increase in the number of available hydroxyl groups, even after the swelling agent has been washed out; again this can be shown most clearly by an examination of moisture sorption. If a sample of cotton after withdrawal from the mercerizing liquor is washed and its desorption curve determined directly from the wet condition, the isotherm shown in Figure 7 [32] is obtained. From this it is clear that cotton immediately after mercerizing, before it has been air-dried, is capable of holding very large amounts of water. But in this condition the number of available hydroxyl groups is so large that as the material is dried many of them become more or less permanently linked to one another, so that they cease to be available as potential absorbing points. This is no doubt the reason why the uppermost curve of this figure is an irreproducible primary desorption curve, and why the subsequent desorption curve obtained after the material has been dried shows that much of the original hygroscopicity has been lost. The same kind of effect is observed in even greater degree in regenerated cellulose while it is still wet, and is one of the reasons why never-dried cellulose film is so much used in research laboratories when it is desired to study cellulose in its most reactive, or most accessible, form.

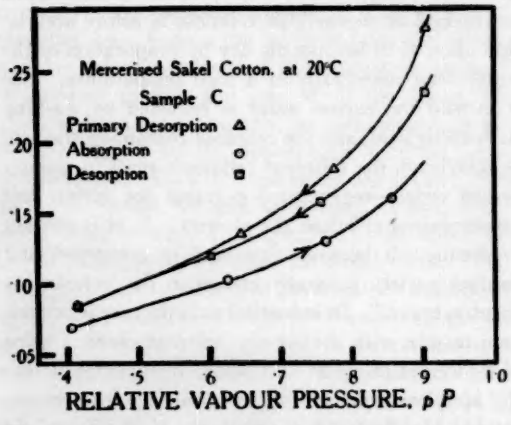
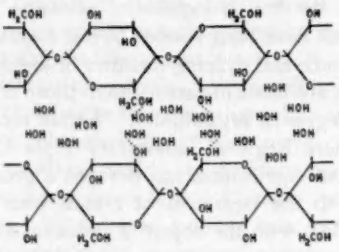
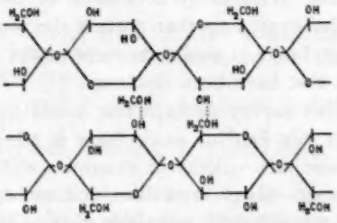


Fig. 7. Grams of water absorbed per gram of dry cotton versus relative vapor pressure.

These considerations make it not unreasonable to assume that although mercerized and regenerated celluloses contain greater proportions of amorphous cellulose than the native material, these amorphous regions may be much more cross-linked, with a range of bond strengths, by hydrogen bonding. In absorbing water vapor or in aqueous media, at least the weaker of these bonds will be broken; hence in respect of reactions in aqueous systems the normal order of reactivity applies. But in the anhydrous systems used for acetylation, these links may very well be maintained unbroken, and on this basis it would not be unexpected that in such systems what we have come to regard as the normal order of reactivity should be reversed. At present, of course, this is little more than speculation—it obviously requires to be tested by studies of the reactivities of these celluloses in media varying in their power to break the postulated bonds—but in the present state of knowledge it is more satisfying than any explanation based on the presence of impurities.

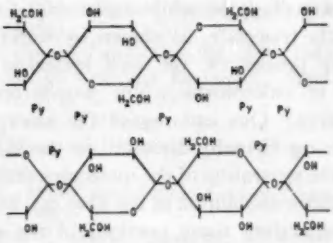


Hydrate cellulose, water-wet

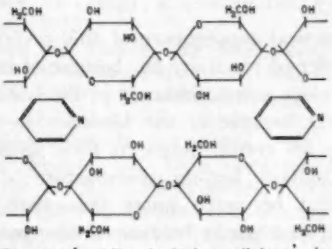


Unreactive mercerised cellulose, dry

Fig. 8. Structural formulas of modified cellulose.



Reactive cellulose, pyridine-wet



Reactive 'pyridine-inclusion-cellulose', dry

Fig. 9. Structural formulas of modified cellulose.

When one comes to examine the other effect—the restoration of the normal order by replacing the water by organic media—the work of the Staudinger school is much more helpful. They have produced several papers [33] on what Staudinger calls "inclusion celluloses." They have found that if the water in a swollen cellulose is replaced by organic liquids in a series where each is miscible with the preceding one, the series may be stopped at any stage, leaving the cellulose still in an open condition and with the extraneous substance so firmly held that it cannot be completely removed even by prolonged heating at 100° C. in a high vacuum. Moreover, this applies even to substances as volatile as acetone. Again this kind of behavior has been familiar to the rayon-producing industry for some time, but it is only now being studied systematically.

The effect of the formation of such "inclusion celluloses" on reactivity is most readily assessed from an examination of some diagrams taken from one of Staudinger's papers. The upper diagram of Figure 8 is a diagrammatic representation of a reactive cellulose, for example, mercerized cotton, in the water-wet state. The lower is intended to show how drying off the excess water produces an inactive cellulose—so-called "hornified" cellulose—by cross-linking of the adjacent chains. But if instead of drying off the excess water we replace it by a water-miscible substance such as pyridine, one obtains the pyridine-wet reactive cellulose represented by the upper diagram in Figure 9. If the pyridine is evaporated from this material, one obtains the pyridine inclusion cellulose shown in the lower diagram, from which the residual pyridine, in amount one molecule per 5–14 glucose residues, cannot be removed for steric reasons alone. In this material all the hydroxyl groups are free, and the cellulose is in consequence highly reactive.

This explanation appears satisfactory when applied to the amorphous regions of cellulose, but Staudinger's view is that in such inclusion celluloses the inclusion occurs between *all* the cellulose molecules, so that there is no difference between the reactivities of crystalline and amorphous regions. The evidence on which he bases this conclusion is that if he partially acetylates an included cellulose and extracts the preparation with chloroform he obtains practically no extract, indicating, in his opinion, that there is no cellulose triacetate present; he therefore concludes that the cellulose chains are evenly acetylated along their length. This conclusion seems to be a complete *non sequitur*. It is easy to stop acetylation of cellulose at a stage at which the crystalline regions remain unchanged cellulose, as shown

by the X-ray diagram, while the amorphous regions are virtually triacetate, as shown by water sorption and dyeing properties, yet such materials have no solubility in chloroform. Nor would one expect them to have. One can regard the amorphous regions as being virtually dissolved in the solvent, but the complete separation of the molecules that is necessary to achieve dissolution of the fiber can be achieved only by separating those portions of the molecules that are held to one another in the crystalline regions. Chloroform cannot do that; it requires a solvent for cellulose.

One practical consequence of this reversal of the normal order of reactivity has become of importance to the cellulose acetate industry in the last decade or two, largely because of the tendency to substitute wood pulp for cotton linters as their source of cellulose. Cellulose for the manufacture of cellulose acetate must be much purer than that used for viscose, at least partly because viscose manufacture involves treating the pulp with fairly concentrated caustic soda solution, which itself removes some of the impurities concerned. Perhaps for this reason the early attempts to prepare acetylation pulps were made by treating viscose-type pulp with 8–10% caustic soda solution. At that concentration virtually no mercerization of cotton occurs, but wood cellulose swells more easily, and in consequence the pulps produced by that method were quite unreactive towards the ordinary acetylation process. An alternative method is to extract the less pure pulp with hot dilute instead of cold concentrated caustic soda. This avoids making the cellulose unreactive, but at least until some years ago was less effective in producing the type of pulp desired. Several satisfactory acetylation pulps are now available, but their makers are not usually overanxious to reveal how they were produced. It may be noted, however, that the pulps made unreactive by cold extraction with concentrated alkali can be activated by boiling with dilute alkali, and a process based on this has been used. There is no sound explanation of this activation; one would assume that it induces a partial reversion towards the condition of native cellulose, but there does not appear to be any moisture-sorption or similar data to support this view. It is worthy of note, however, that wet cotton after a boil of this kind shows the same kind of irreproducible primary desorption curve that was illustrated previously for mercerized cotton, though on a lower level of hygroscopicity; evidently, therefore, the boil is capable of releasing hydroxyl groups that have been bonded to one another.

The handle and draping qualities of highly crystalline fibers are less satisfactory than those of fibers of a lower degree of crystallinity. Within recent years the Southern Regional Laboratory of the U. S. Department of Agriculture has devoted a good deal of attention to the treatment of cotton with aliphatic amines [34], with the object of reducing its crystallinity, therefore improving some of its textile qualities. The process appears to involve a swelling of the cellulose followed by a removal of the swelling agent under conditions that prevent the formation of cross-links, hence is similar to some of the activation processes that have been discussed.

From this survey perhaps one lesson may be derived. In this field of work there is often a great deal of loose talk—plenty of examples will be found in this paper—about crystalline and amorphous regions, inaccessible and accessible regions, unreactive and reactive celluloses. But where there is no clear-cut dividing line, but rather a gradual transition, between crystalline and amorphous regions it is surely not surprising to find that the so-called crystalline–amorphous ratio varies according to the particular method used to determine it. Again, has one any right to expect that the accessibility of cellulose to acetic anhydride shall be the same as its accessibility to helium? If not, what is meant by the "accessibility" of a cellulose? With regard to reactivity the position is even more complicated. There are a few reactions that have not been discussed at all—reactions such as nitration, where the nitrating agent, the nitronium ion, is able to penetrate the crystalline as well as the amorphous regions, so that the reaction occurs homogeneously throughout the material. For such reactions the concept of accessibility, and even of reactivity as it has been used here, is meaningless. But even for reactions of the type under consideration, where the crystalline regions are not initially penetrated by the reagents, it is dangerous to make simple generalizations. The acid-hydrolysis method of measuring reactivity has been much criticized; but when all has been said against it, one would expect that it would be at least as good a method as any other for assessing the reactivity of cellulose towards acid hydrolysis. This emphasizes the point that there is probably no particular harm in loose talk of this kind so long as it is recognized as such.

But the literature of this field reveals a strong tendency to generalize specific quantities determined under specific conditions and promote them to the status of intrinsic properties. It therefore behooves all textile chemists to recognize that cellulose behaves as different substances in different media and under different conditions, and to resist all attempts to generalize too freely from behavior under specific circumstances. By doing so we may help to remove a substantial impediment to further progress.

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The Effect of Silicone Softeners on Resin Treated Cottons[1]

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Abstract

A brief discussion is given on the mechanism by which textile softeners produce their effects. Differences in this respect between silicone softeners and the conventional long chain fatty acid types are pointed out. Also, some of the applications of silicone softeners with respect to cotton are discussed. The results of a study on the effects of silicone and conventional organic softeners on the physical properties of resin treated cottons are given. In this study several well known types of softeners were included in three typical minimum care resin treatments. Their effects on the tear strength, tensile strength, wrinkle recovery, abrasion resistance, and sewing lubrication were noted, with special reference to laundering durability. Based on the products evaluated, the data indicate the silicone softeners increase wrinkle recovery and some of the other physical property values above those imparted by the organics. This increase in efficiency leads to the conclusion that the amount of resin used could be decreased, still giving acceptable wrinkle recovery values and at the same time increasing the rest of the physical property values.

Introduction

Among the many advances in textile chemical technology in recent years, the successful application of resin to cottons is certainly one of the foremost. The finishing industry is by now quite familiar with the various thermosetting resins and their effects on cotton. Their ability to chemically modify cellulosic fibers has resulted in enthusiastic consumer acceptance of what are often referred to as "wash and wear" cottons.

The chemistry of the thermosetting resins as applied to cottons will not be covered, as there are many excellent articles available on this subject. Let it suffice to say that along with the many indisputable advantages they impart to the cellulosics, there are a few deficiencies. These are primarily due to a loss in extensibility of the fiber upon being cross-linked by the resin. This results in reduced physical strength and at times in a poor hand; finishers have attempted to overcome these deficiencies by the addition of a softener.

The function of the softener in this application is to modify or soften the hand and to regain, at least in part, the lost physical properties. The softener accomplishes this by promoting interfiber lubricity; a good softener must be a good lubricant. Of course, other factors also should be considered, such as durability, cost, and nondiscoloration of the fabric.

Although there are many softening preparations commercially available, by far the most common are those based on long chain fatty compounds such as sulfated tallows or oils. In this instance the fatty residue provides the softening or lubricating action. This type of softener lies on the outer surface of the fiber and is not chemically linked as is the resin. Since no permanent bonding exists, there is little to hold the organic molecule on the fiber during the dry cleaning or laundering of the fabric.

Silicones are a comparatively recent step in the evolution of softeners. Finishers who had previously known silicone emulsions only as durable water repellents found that they could impart many desirable characteristics to fabrics if they used them as softeners.

Chemically, the silicone fluids used in these emulsions are blends of two silicone polymers; dimethylpolysiloxane

$$(CH_3)_3Si{-}O{-}\left[\begin{matrix}CH_3\\ Si{-}O\\ CH_3\end{matrix}\right]_n{-}Si(CH_3)_3$$

[1] Presented at the Sixth Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., October 2, 1957.

where $n = 500$–600 units, and methylhydrogenpolysiloxane

$$(CH_3)_3Si—O—\left[\begin{matrix}H\\Si—O\\CH_3\end{matrix}\right]_n—Si(CH_3)_3$$

where $n = 40$–60 units. Each of these fluids fulfills a particular function in the softener structure. The dimethylpolysiloxane is generally credited with the lubricating characteristics by virtue of its many organic groups, while the methylhydrogenpolysiloxane contributes durability. The latter is accomplished by the hydrolysis and condensation of some of the available silane hydrogens to form a siloxane–oxygen cross-linkage. When this step is accomplished after application to a fabric, it results in a tough, transparent, hydrophobic, pliable film encasing each individual fiber. Although this cross-linking reaction will occur due to heat alone, the speed and degree of cross-linking are enhanced by the addition of small amounts of catalysts. Usually metallic compounds such as zinc or tin salts are used. When the finisher wants water repellency, a catalyst is used. However, for hand or softening effects only, the catalyst is often omitted.

Another difference between the water repellent application and the softener application is the amount of silicone applied. For water repellency the treating bath is generally adjusted so as to deposit 1.0% or more silicone solids on the fabric, while for softeners this figure is 0.5% or less.

The silicone "skin" that is formed around the fiber is insoluble in water and in the common dry cleaning solvents. Therefore, the silicones should be more durable than the organic type softeners. However, durability alone is not enough. As previously mentioned, a softener's lubricating properties are of prime importance in helping to regain some of the lost physical strength of a resin treated cotton. Several lubricity studies have been undertaken comparing silicone oils with organic oils. Tabor and Hansen, in comparing the two types of oils at the same viscosity, demonstrated that the silicones exhibited an appreciably lower coefficient of friction under conditions of hydrodynamic lubrication [3]. This work was accomplished with nylon yarn and nylon and Dacron [2] monofilaments. Currie and Hommel have shown the superior characteristic of silicone oils vs. organic oils as a lubricant for nylon under conditions of boundary lubrication [1]. While none of the above work was performed directly on cotton, it does reflect on the inherent lubricating characteristics of the fluids.

In actual practice, the finisher has found many uses for silicone softeners on a wide variety of fabrics, ranging from flannel to tricot. They are also being used as napping softeners and lubricants for the brushing operation. They are preferred on naphthol-dyed cottons since they don't appear to effect shade changes or crocking as much as the organics. Also, they are applied as a pretreatment prior to schreinering or embossing. Another application in which silicones make one of their greatest contributions as softeners is in resin formulations. It was felt that because of the growing importance of the resin-type finish and because of the lack of silicone softener information, further data in the field should be obtained. Therefore, the purpose of this investigation is to compare the effects of the various silicone and organic softeners on the physical properties of cotton treated with typical resin formulations.

Experimental

The fabric used in this study was 39-in. 80/80, 4.00 oz./yd. mercerized cotton print cloth. This was considered representative of the fabric ordinarily used in wash and wear finishing. Although many different resin–softener combinations were tried, the majority of this work is with three typical resin combinations:

1. Blend of dimethylol ethylene urea (DMEU) and methylated methylol melamine.
2. Blend of DMEU and acrylic resin.
3. Blend of DMEU and polyvinyl alcohol (PVA).

An organic amine-type catalyst was used to catalyze the resins. Each of the three resin blends was used in conjunction with four or five softeners plus a control. There are hundreds of commercially available organic softeners, and to include all of these would make the evaluation impractically long. This study was therefore limited to three of the more widely used organics: one cationic, one anionic, and one nonionic. Various nonionic silicone emulsions without catalyst were also used as softeners. In separate evaluations, some of the silicone emulsions were evaluated with a silicone-curing catalyst in addition to the resin-curing catalysts.

[2] Du Pont trademark.

Table I gives the various finishing agents and the percentages used. The concentrations used were taken from commercial practice and represent comparable costs of the silicone and organic softeners.

The fabric was padded in a three-roll Butterworth 10-in. laboratory pad using a single-dip, single-nip threading with a roll gauge pressure of approximately 40 lb. This pressure gave approximately 75% wet pick-up. The fabric was then dried at 160° F. and cured at 300° F. for 7 min. To avoid any premature removal of softeners, the afterwash was omitted.

Since this investigation is primarily a study of softeners and their effects, their durability is an important factor to consider. For this reason, the first set of physical tests was run without any laundering or scouring; the other tests after one, three, and five launderings. Except where otherwise specified, the launderings were carried out in a Westinghouse home washer and dried in a Westinghouse drier to simulate home laundering conditions. The following tests were conducted in accordance with Federal Specification CCC-T-191*b* [2]: tensile strength (Method 5104) on the Scott Tester, tear strength (Method 5132) on the Elmendorf Tear Tester, flex abrasion resistance (Method 5200) on the Stoll Flex Machine, and crease resistance (Method 5212) on the Monsanto Wrinkle Recovery Tester. All tests were conducted at 70° F. and 65% relative humidity after the samples had been conditioned for at least 12 hr.

TABLE I. Product Concentrations

Resins	
DMEU-Melamine blend 3 : 1 solids ratio DMEU-Acrylic blend 3 : 1 solids ratio DMEU-Polyvinyl alcohol blend 3.5 : 1 solids ratio	Each blend resulted in approximately 8% resin solids on the fabric unless otherwise indicated.
Organic softeners	
Anionic softener Cationic softener Nonionic softener	All the organic softeners were padded along with the resin from a 3.0% bath concentration with a 75% wet pickup resulting in approximately 2.2% softener as received on the fabric.
Silicone softeners	
Syl-soft 10 Syl-soft 12	Syl-softs 10 and 12 were padded along with the resin from a 2.1% bath with a 75% wet pick-up resulting in approximately 1.6% as received on the fabric. This deposits about 0.5% silicone solids on the fabric.
Dow Corning 104	The DC 104 was padded along with the resin from a 1.6% bath with a 75% wet pick-up resulting in approximately 1.2% as received on the fabric. This deposits about 0.5% silicone solids on the fabric.
Catalysts	
Organic amine type resin catalyst	15% catalyst based on the weight of the resin solids.
XEY-21 Silicone catalyst	20% catalyst based on the weight of DC 104 Emulsion as received.
XEY-21 Silicone catalyst	15% catalyst based on the weight of Syl-softs 10 and 12 as received.

In addition to the standard tests, two resin formulations were evaluated in sewing tests: the DMEU-melamine and DMEU-acrylic formations. Each of these resin blends was studied alone and in combination with one silicone and one organic softener. The latter were selected on the basis of their performance in preceding tests. The sewing tests themselves were of the yarn-severance type and were conducted before and after one laundering. They were performed on three layers of fabric laid one upon the other with the warp and fill yarns of all the pieces running in the same directions. The plies were then sewn together with two rows of single-lock stitches approximately ½ in. apart. The seams were in the shape of an "L", with each leg about 15 in.

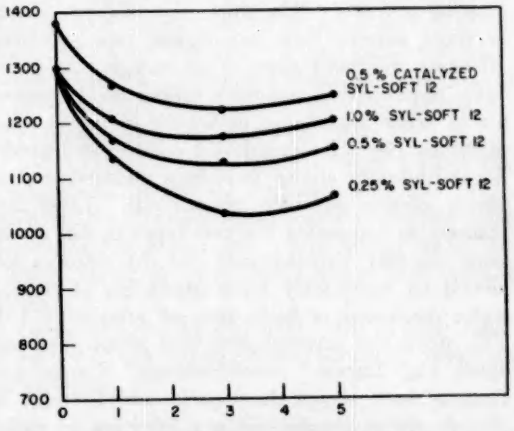

Fig. 1. Tear strength, DMEU-melamine blend. Sum of warp and fill (g.) vs. percent solids on fabric.

long, so that the stitches ran parallel to both the warp and the filling. The stitching was done with a No. 4 needle using approximately 12 stitches/in. The sewing machine (a 31–15 Singer) was run at 3200 r.p.m. to obtain maximum cutting. Earlier tests indicated that a high speed such as this was necessary to obtain a comparison of the lubricating properties of the softeners. The last 3 in. of the middle layer of fabric of the second row of stitching in both the warp and fill direction were then inspected for the number of cut threads and tabulated as percent thread severance. This testing procedure is similar to that recommended by the Textile Distributors Institute, Inc. [4] and to Federal Specification CCC-T-191*b*, Method 5400 [2].

Discussion

As previously mentioned, the softener concentrations used were taken from commercial practice and represent comparable costs. It might be well to elaborate a bit on this point before proceeding, since silicones are considered by some as more expensive to use than other types of softeners. One of the interesting things about silicones is that the physical property values that are imparted to the fabric change very little within wide concentration variations. Although most of this work is based on 0.5% silicone solids on the fabric, it was found that similar results will be obtained whether this amount is 1.0% or 0.25%. This is demonstrated in Figure 1.

In addition, one may increase most of the physical property values by increasing the degree of cross-linking of the silicone. An example of this is also presented in Figure 1, where the catalyzed 0.5% concentration gives higher tear strength values than the

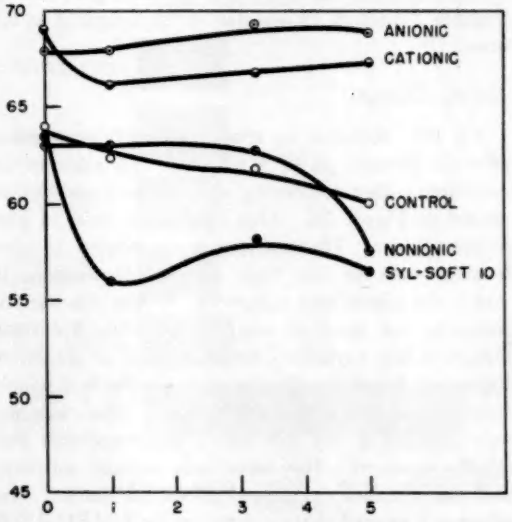

Fig. 3. Tensile strength, DMEU-acrylic blend. Sum of warp and fill (lb.) vs. number of launderings.

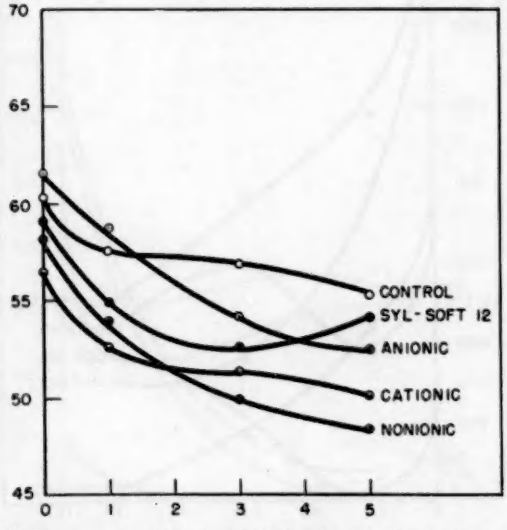

Fig. 2. Tensile strength, DMEU-melamine blend. Sum of warp and fill (lb.) vs. number of launderings.

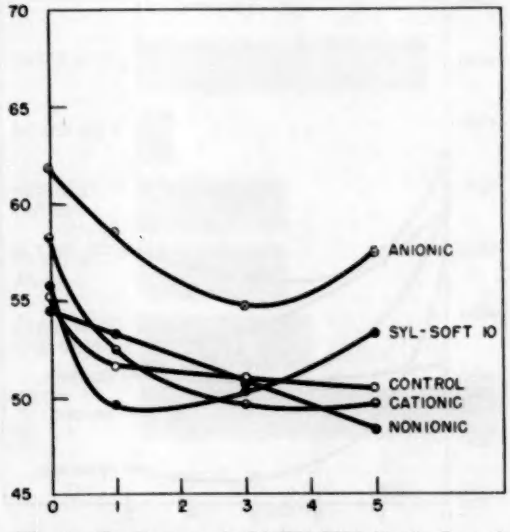

Fig. 4. Tensile strength, DMEU–PVA blend. Sum of warp and fill (lb.) vs. number of launderings.

uncatalyzed 1.0% concentration. It thus becomes apparent that one may decrease the amount of silicone used to a point where its cost per unit area of fabric is equal to or less than that of the organic softeners. At the same time, the treated fabric will retain the physical property advantages of the silicone shown at higher concentrations.

The results of the tests are graphically presented in Figures 2 through 19 and may be summarized as follows.

Tensile Strength

An 8% decrease in tensile strength was noted after the addition of 0.5% silicone solids alone to the untreated cotton and curing in the normal manner, as shown in Figure 16. This loss is due only in part to the silicone. The rest may be attributed to other factors, such as the high curing temperature to which the cotton was subjected. When the various softeners are used in conjunction with the resin blends, a few variations were noticed, as shown in Figures 2, 3, and 4. The anionic gave the best tensile strength values in all formulations. This was the only instance in any test that a single softener was clearly superior. The other two organic softeners and the silicones performed about the same. The silicones appeared slightly better in the DMEU–PVA and DMEU-melamine formulations from a durability standpoint. A point of interest lies in the noticeable drop in tensile strength values of the silicone treated samples after the first laundering. Thereafter the results are fairly constant. This was generally true of all the physical tests. The organic softeners, on the other hand, do not always demonstrate this tendency to level out after the initial laundering.

Tear Strength

A 20% increase in tear strength was noted after the addition of 0.5% silicone solids alone to the untreated cotton and curing in the normal manner, as shown in Figure 17. When the softeners are used with the resin blends, the silicones generally appear to give higher tear strength values and better durability than the organics, as shown in Figures 5, 6, and 7. Only in the DMEU–PVA formulation did an organic (the cationic) appear superior. The decrease in organic durability is especially noticeable in the DMEU-melamine formulation. In some cases the organic tear strength values were below that of the no-softener control after five launderings. The

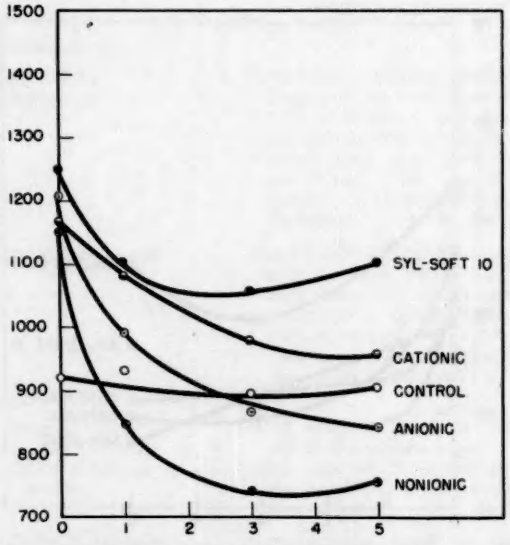

Fig. 5. Tear strength, DMEU-melamine blend. Sum of warp and fill (g.) vs. number of launderings.

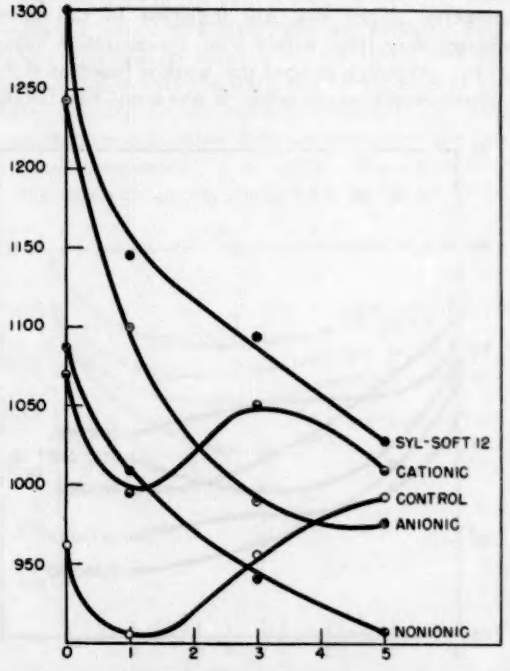

Fig. 6. Tear strength, DMEU-acrylic blend. Sum of warp and fill (g.) vs. number of launderings.

no-softener control remained fairly constant throughout the five launderings.

It may be well to point out at this time the durability of the silicones under extreme conditions. As a side evaluation, several samples of the test cotton were treated, adding 5% DMEU solids with several softeners and 5% straight urea formaldehyde using the same softeners. The samples were then subjected to 25 40-min. launderings in a reversing wheel type machine at 160° F. The results of this evaluation are given in Figures 8 and 9. The uncatalyzed silicones gave slightly higher tear strength than the organics, though in both instances a comparison with the controls indicated that most of the softener was removed. The catalyzed silicones, however, demonstrated superior durability. With both types of resins the catalyzed silicones gave tear strength values approximately 50% higher than the resin treated controls.

Flex Abrasion

A 70% increase in abrasion resistance was noted after the addition of 0.5% silicone solids alone to the untreated cotton and curing in the normal manner, as shown in Figure 18. When the softeners are used with the resin blends, however, the organic-softened samples appeared substantially superior, as shown in Figures 10, 11, and 12. They demonstrated higher flex values, and equal or superior durability in the DMEU–PVA and DMEU-acrylic formulations, compared to the silicone emulsions. The organics and the silicones exhibited approximately the same values in the DMEU-melamine formulation. As may be observed, the general durability trend is a slight increase after the initial laundering drop. This is in

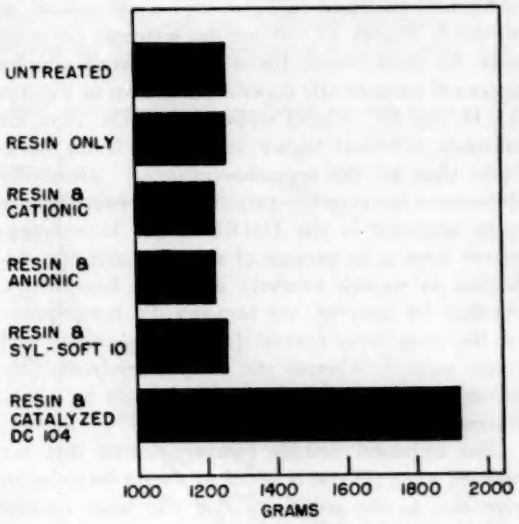

Fig. 8. Tear strength values after 25 launderings, 160° F., reversing wheel, 5% urea formaldehyde resin.

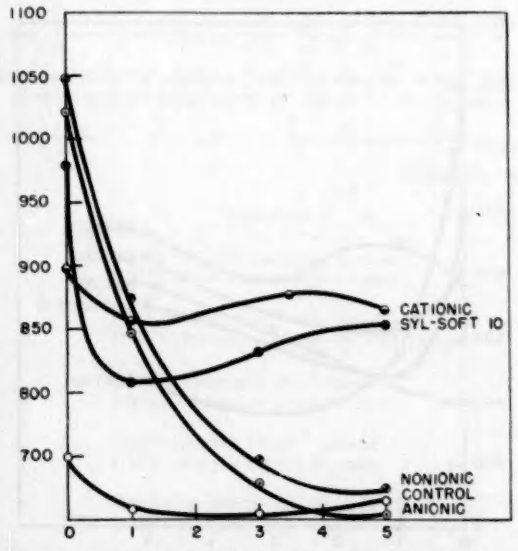

Fig. 7. Tear strength, DMEU–PVA blend. Sum of warp and fill (g.) vs. number of launderings.

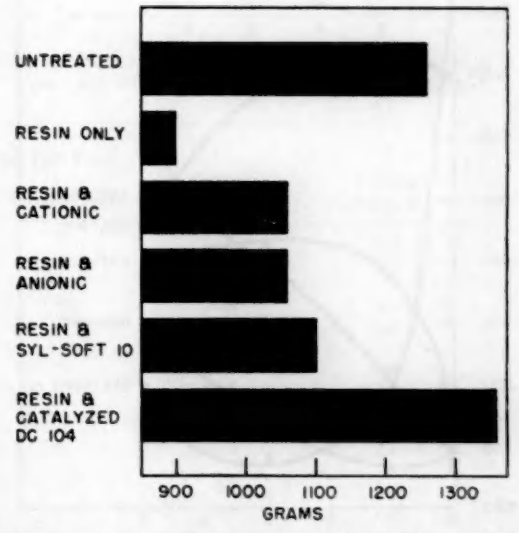

Fig. 9. Tear strength values after 25 launderings, 160° F., reversing wheel, 5% DMEU resin.

contrast to the no-softener control, which demonstrated varying degrees of decreasing values with increasing launderings.

Wrinkle Recovery

A 15% increase in wrinkle recovery was noted with the addition of 0.5% silicone solids alone on the untreated cotton and curing in the normal manner, as shown in Figure 19. When the softeners are used with the resin blends, the silicone softened samples appeared substantially superior, as shown in Figures 13, 14, and 15. Almost without exception, all of the silicones exhibited higher values and better durability than all the organics evaluated. Durability differences between the two classes of softeners are quite apparent in the DMEU-acrylic formulation, where there is an average of approximately 60° difference in wrinkle recovery after five launderings. As may be observed, the organics did not improve on the no-softener control (and in some cases had lower values), whereas the silicones generally improved on the control (in many instances by a substantial margin).

The increased wrinkle recovery values that are realized when silicone is added to a resin formulation give rise to the possibility that the resin content could be decreased somewhat and still retain high enough wrinkle recovery to qualify as wash and wear. (A finish that can give wrinkle recovery values of 250° is generally considered a good crease resistant finish.) Thus, by decreasing the amount

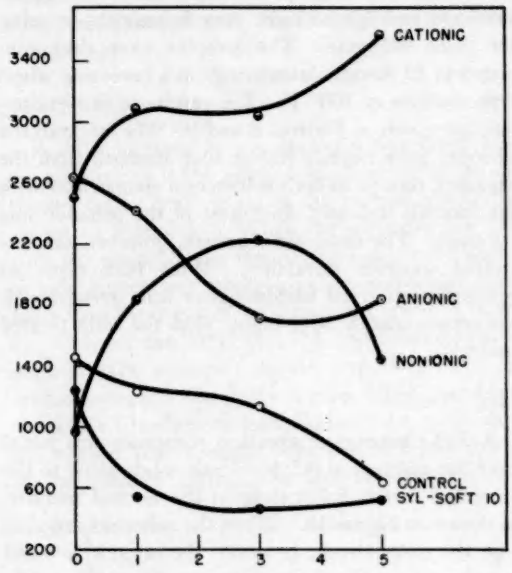

Fig. 11. Flex abrasion, DMEU-acrylic blend. Sum of warp and fill cycles vs. number of launderings.

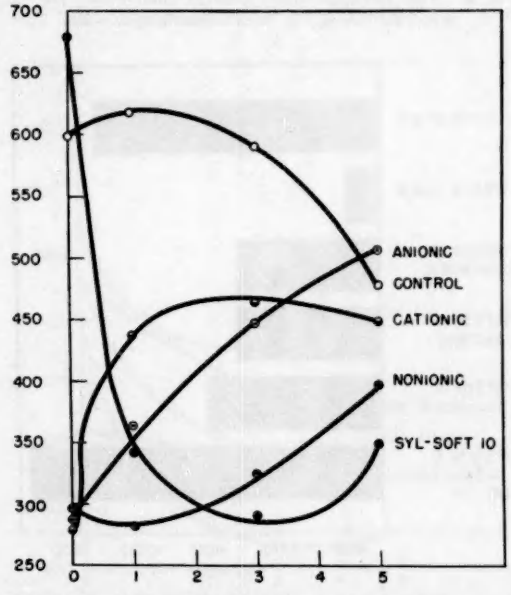

Fig. 10. Flex abrasion, DMEU-melamine blend. Sum of warp and fill cycles vs. number of launderings.

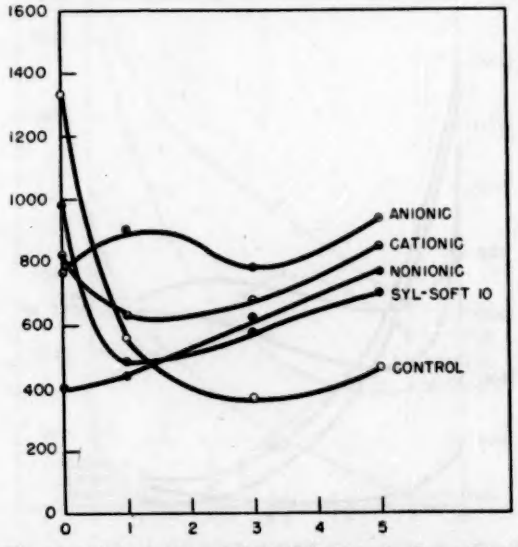

Fig. 12. Flex abrasion, DMEU–PVA blend. Sum of warp and fill cycles vs. number of launderings.

of resin, the other physical property values would be improved; it is with this thought in mind that Figures 16 through 19 are presented. In each of these physical property figures appear curves representing 8.0% resin solids, or a typical "full" wash and wear formulation. This was then dropped to 4.0%, holding the silicone softener constant at 0.5%, and finally dropped to 0% resin and 0.5% silicone. These large decreases in resin percentages are not meant to be given as recommendations, but are merely convenient figures to help illustrate the net effect of the silicone addition–resin reduction trend.

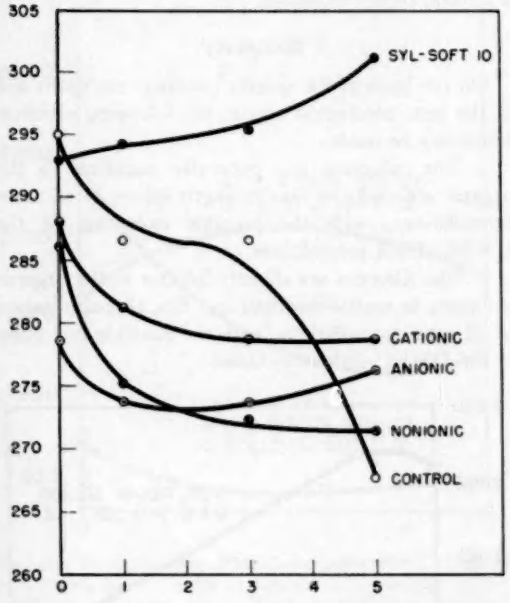

Fig. 13. Wrinkle recovery, DMEU-melamine blend. Sum of warp and fill angle values vs. number of launderings.

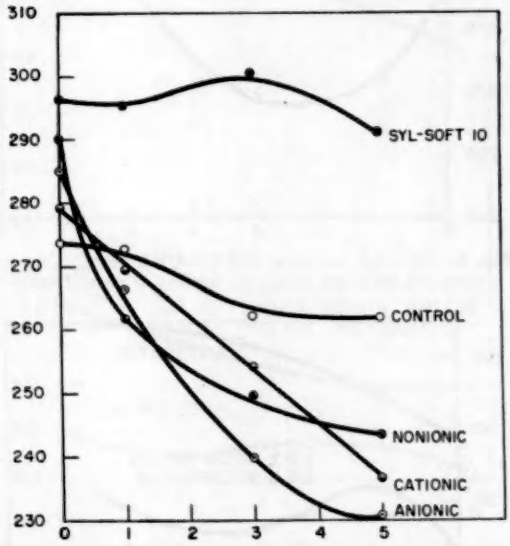

Fig. 14. Wrinkle recovery, DMEU-acrylic blend. Sum of warp and fill angle values vs. number of launderings.

Sewing Tests

The results of the sewing tests are presented in Table II. As would be expected, the control samples (those without any softener for lubrication) showed the highest percentage of thread cutting both

TABLE II. Sewing Test Data

Treatment	Launderings	Cutting fill, %	Cutting warp, %
DMEU-Melamine blend—cationic	0	31.6	1.3
DMEU-Melamine blend—cationic	1	38.8	2.5
DMEU-Melamine blend—Syl-soft 12	0	20.4	1.2
DMEU-Melamine blend—Syl-soft 12	1	25.8	1.3
DMEU-Melamine blend—control	0	47.7	4.6
DMEU-Melamine blend—control	1	43.8	2.5
DMEU-Acrylic blend—cationic	0	46.3	1.3
DMEU-Acrylic blend—cationic	1	33.8	2.5
DMEU-Acrylic blend—Syl-soft 12	0	9.2	0.4
DMEU-Acrylic blend—Syl-soft 12	1	20.4	2.5
DMEU-Acrylic blend—control	0	46.3	4.0
DMEU-Acrylic blend—control	1	51.7	3.3

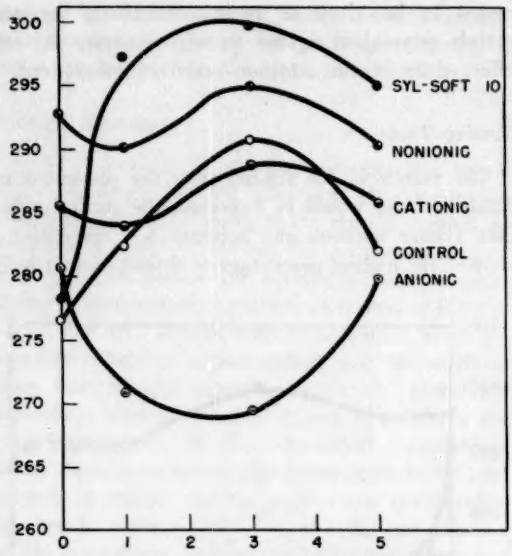

Fig. 15. Wrinkle recovery, DMEU–PVA blend. Sum of warp and fill angle values vs. number of launderings.

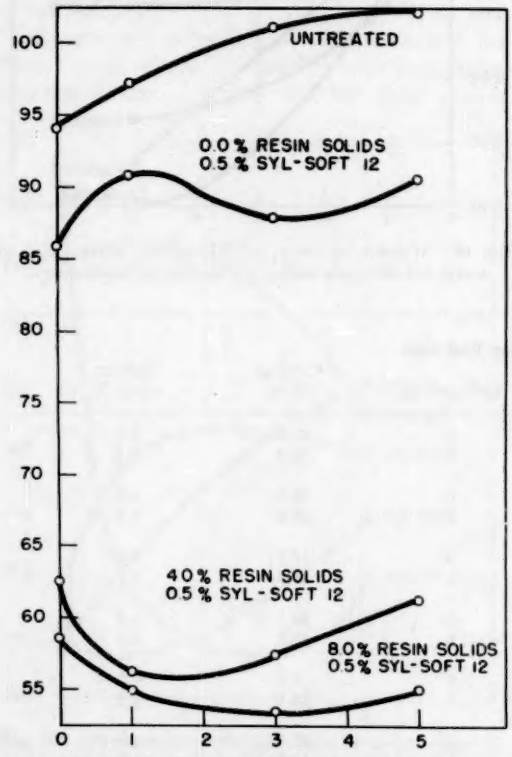

Fig. 16. Tensile strength, DMEU-melamine blend. Sum of warp and fill (lb.) vs. number of launderings.

before and after one laundering. Those samples utilizing the silicone showed less thread cutting than those samples utilizing the cationic softener. In some instances, (i.e., DMEU-acrylic formulation, zero launderings, fill direction) this margin was of a rather large magnitude. In both the silicone and the organic softened samples, a slight increase in thread cutting was recorded after one laundering, which would be expected if the laundering removed a portion of the lubricant.

Summary

On the basis of the specific products evaluated and of the tests conducted herein, the following observations may be made.

1. The silicones are generally superior to the organic softeners in tear strength values in all resin formulations, with the possible exception of the DMEU–PVA formulation.

2. The silicones are slightly inferior to the organic softeners in tensile strength and flex abrasion values in all resin formulations, with the possible exception of the DMEU-melamine blend.

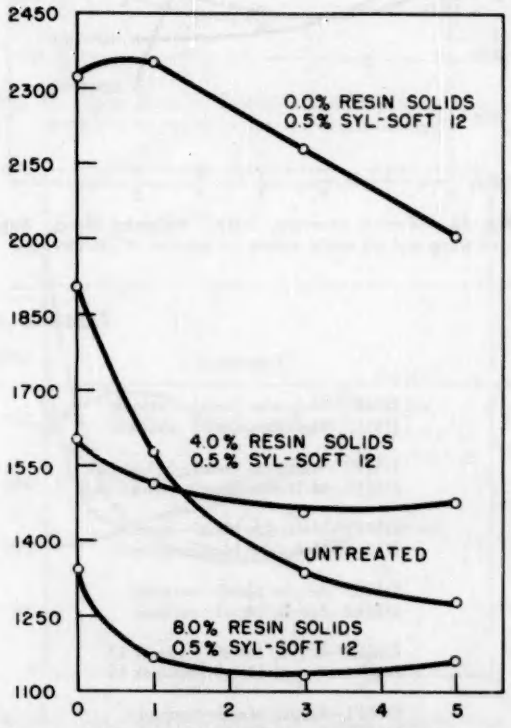

Fig. 17. Tear strength, DMEU-melamine blend. Sum of warp and fill (g.) vs. number of launderings.

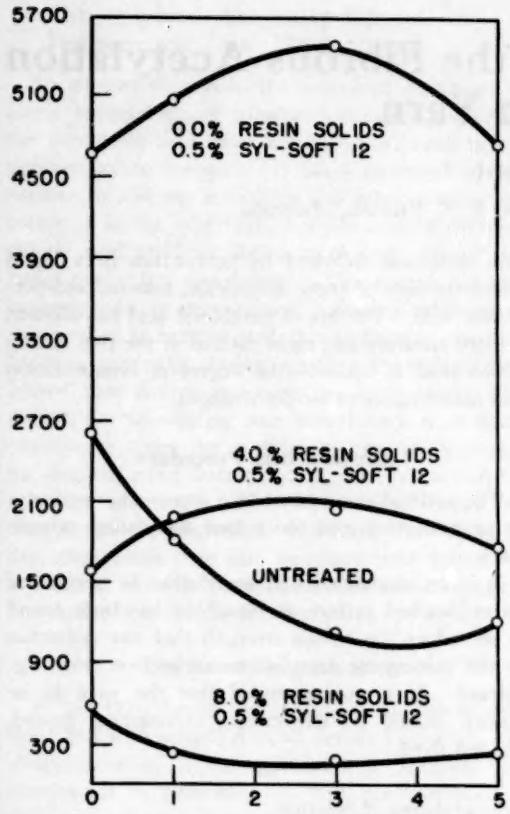

Fig. 18. Flex abrasion, DMEU-melamine blend. Sum of warp and fill cycles vs. number of launderings.

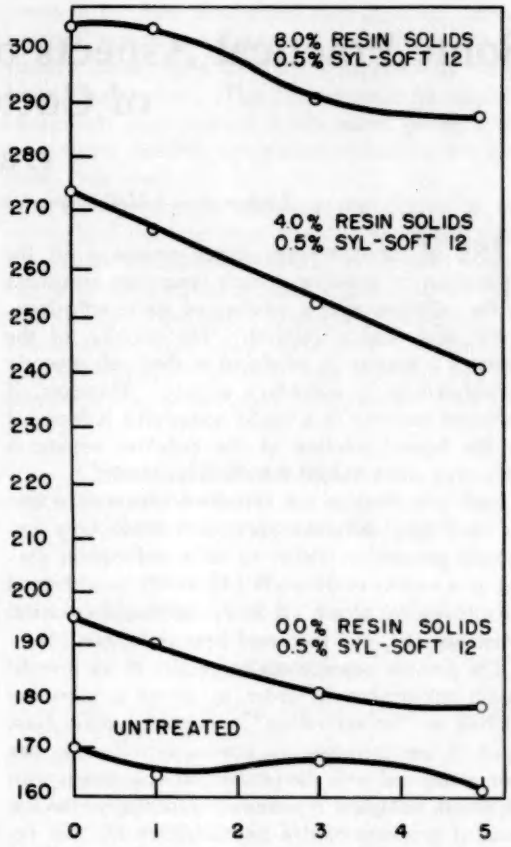

Fig. 19. Wrinkle recovery, DMEU-melamine blend. Sum of warp and fill angle values vs. number of launderings.

3. The silicones are definitely superior to the organic softeners in wrinkle recovery values in all resin formulations evaluated.

4. The catalyzed silicones generally give higher values and superior durability in comparison with the uncatalyzed silicones.

5. The silicone softener is superior to the organic softener as a sewing lubricant in both resin formulations evaluated.

6. Silicones make the greatest overall improvement in the fabrics' physical properties when used with the DMEU-melamine finish, and the least improvement when used with the DMEU–PVA finish.

7. Based on the increased wrinkle recovery efficiency obtained by using silicones, the amount of resin could be decreased, still imparting acceptable wrinkle recovery values. The reduction in resin deposition would then in turn allow the remaining physical property values to increase.

Acknowledgments

The author wishes to express his sincere appreciation to those persons and companies who contributed technical information, materials, and other services to this study. Special thanks are extended to the Cranston Print Works, The Dow Chemical Company, Monsanto Chemical Company, and Rohm and Haas Company.

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Some Practical Aspects of the Fibrous Acetylation of Cotton Yarn

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ONE of the customary stages necessary for the production of cellulose acetate comprises treatment of the cellulose with a mixture of acetic anhydride, acetic acid, and a catalyst. The solution of the primary triacetate so produced is then subsequently hydrolyzed to a secondary acetate. However, if sufficient quantity of a liquid nonsolvent is included in the liquor, solution of the cellulose acetate is prevented and a fibrous esterification results.

Such esterification can transform cotton yarn into an essentially different fiber with some very important properties: ability to resist subsequent dyeing by a variety of dyestuffs [4], ability to withstand microbiological attack [2, 3, 7], increased electrical resistance [6], and increased heat resistance [5].

The present paper contains results of an investigation undertaken in order to secure a yarn exhibiting an "immunization" to certain specific dyes. Most of the literature on fibrous esterification has been concerned with the production of a cotton with improved biological resistance; accordingly, the associated property of dye immunization has not received much attention.

The bath for heterogenous acetylation usually consists of acetic anhydride, a nonsolvent (e.g., toluene), and an acid catalyst (e.g., sulfuric or perchloric acid). To produce an acetylated fiber from cotton yarn, important considerations are the retention of fiber strength and fiber count; both these factors must be balanced against the degree of immunization desired.

The first experiments were performed on various undyed samples of mercerized and unmercerized cotton according to the directions given in patents granted over twenty years ago [1]. In some instances, slight immunizing to several direct cotton and silk dyes was obtained, while in cases where very successful resist effects were obtained the loss of tensile strength was so great that the yarn could not be subsequently knitted.

The process to be reported is similar in principle to preceding methods, which involve an acid activation treatment followed by acetylation in a liquid which consists of acetic anhydride, toluene, and perchloric acid. The use of perchloric acid has allowed a more accurate and rigid control of the two factors which tend to oppose—the degree of immunization and maintenance of tensile strength.

Experimental Procedure

The method consists of two steps—the preacetylating activation and the actual acetylation process itself.

It is recommended that acetylation be performed on unbleached cotton, as bleaching has been found to so reduce the tensile strength that any reduction by the subsequent acetylation can become more significant. It is recommended that the yarn to be treated should be mercerized, unbleached, gassed, and vat dyed.

Preacetylating Activation

The treatment with glacial acetic acid presented little difficulty once a satisfactory liquor/yarn ratio had been determined. The skeins of yarn to be treated are well beaten out by hand and then immersed in glacial acetic acid for 1 hr., during which time they should be kept well agitated. The liquor/yarn ratio is not extremely critical, but it is better to use an excess; approximately 2 l. of acid/4-oz. skein is required. At the end of the hour the skeins are removed, allowed to drain, and excess acid thoroughly removed (this can be performed with an ordinary clothes wringer set to exert the maximum pressure between the rollers.) The squeezed-out skeins should then be hung loosely until immersed in the next bath, which can be prepared while the yarn is being treated in the acid.

Acetylation

Yarn	4 oz. skein
Acetic anhydride	666 ml.

Toluene (commercial grade) 1334 ml.
Perchloric acid (A.R. 70%) 0.8 ml.

To prepare this bath, the measured quantities of acetic anhydride and toluene are mixed together; the perchloric acid must not be added until a few minutes before the yarn. It has been found advantageous to mix the anhydride and toluene while the cotton is in the acid bath, but not to add the perchloric acid until all skeins have been wrung and hung ready for acetylating. The perchloric acid concentration is very critical. During addition of this acid it is noticed that the acetylating mixture becomes gradually darker, passing through a dark brown, then a deep red color to almost black. Although no time factor has been found, it is usual practice to allow the acetylating mixture to attain its deepest color before adding the yarn. After thorough agitation for 35 min. the liquor is run off. The skeins are allowed to drain and then hung to dry, after which they may be rinsed with water. If considered desirable, use of a cationic softening agent may assist in providing a softer yarn.

Degree of Immunization

It has been found that with the procedure outlined and with attention to all details (especially the maintenance of liquor agitation) a complete immunization is achieved. A test piece should be dyed in a mixture of the dyes concerned, the degree of dyeing being judged by the required depth of shade obtained on unimmunized yarn.

It has been found that the untreated initial cotton used in these experiments had a tensile strength of 300–350 g.; after immunization the figure remained within this range. In some cases where yarn had a tensile strength below this figure, it still knitted satisfactorily and was acceptable in use. The count of the final immunized yarn is of the utmost practical importance, because if the threads are too swollen considerable difficulty is experienced during knitting operations. This feature must be carefully controlled; with yarn of 2/70s initial count it has been found that this figure must remain higher than 2/60s final count.

It is important in assessing the degree of immunization that the dyes used be specified; while some of the methods described in the original patents may give resist effects against certain unstated dyes, they have not been found to give a resist against the following six dyes which were currently employed in a silk–rayon combination hose in which two immunized cotton stripes were incorporated. The dyes were:

Chlorantine F. Red 6 BLL
Durazol Blue 2 R.S.
Chlorantine Fast Orange 2 GLL–125%
Silk Brown R
Neutral Yellow RX
Acid Milling Black B

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Manuscript received November 7, 1957.

Letters to the Editor

Ultraviolet Irradiation and the Wool Fiber Epicuticle

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Commonwealth Scientific and Industrial Research Organization
The Hermitage
338 Blaxland Road, Ryde, N.S.W., Australia
October 9, 1957

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

It has been known for many years that one of the effects of ultraviolet radiation on wool is to increase the rate of uptake of some dyes. Other treatments which produce a similar result include modification of the wool by alkali, by acid, and by chlorination. Lindberg [3] concluded that reaction of alkali and acid with the fiber epicuticle was responsible for the increased rate of dye uptake in these cases.

The following experimental results suggest that in the case of ultraviolet irradiation of wool it is again modification of the epicuticle which is primarily responsible for the accelerated rate of dye uptake. Pieces of fibers were abraded between two glass slides whose surfaces had been roughened by grinding with a fine abrasive powder. Abrasion was continued until all cuticular material was removed. The pieces were then cut in halves; half was irradiated for a time known to give a large increase of dyeing rate in intact fibers (2 hr. at 15 cm. from a 125 watt, high pressure, mercury in quartz lamp). The irradiated and unirradiated pieces were immersed in dye at room temperature on the same microscope slide and examined at intervals for depth of color. Both irradiated and nonirradiated pieces appeared to dye at approximately the same rate, and were heavily dyed before an intact fiber on the same slide had achieved any appreciable coloration. It thus appears that if ultraviolet light affects rate of dye absorption by the wool fiber cortex the effect is secondary to modification of the cuticle.

In another experiment intact fibers were treated for 10 min. in a 2% wt./vol. butanolic KOH solution. This treatment is believed to affect only a region close to the fiber surface [3, 4]. Some of these fibers were then irradiated. On subsequent dyeing it was found that again the irradiated and nonirradiated fibers dyed at approximately the same rate.

The epicuticle was not destroyed by irradiation. This was demonstrated by the fact that Allworden blisters formed on fibers immersed in saturated bromine water after the fibers had been irradiated under the conditions stated above. However, the time required for the blisters to form was substantially increased (from a few minutes to about 2 hr.) and their appearance was different. Normal fibers in general give large, discrete blisters. The irradiated fibers were characterized by less numerous and smaller blisters; in some cases the membrane was lifted over the length of several adjacent scales, forming a long, low blister with indentations at the positions of the underlying scale edges.

Lindberg [3] observed that one of the effects of aqueous alkali on wool was to delay the Allworden reaction. He concluded that the delay was not due to the increased permeability of the epicuticle, but that bromine water reacted less rapidly with alkali-treated wool than with untreated wool. To check whether this was the case here, irradiated and normal wool samples, each of mass 1 g., were treated for 15 min. in saturated bromine water. In this time the Allworden blisters were fully developed in the normal wool, but no blisters appeared in the irradiated wool. The samples were then washed for 15 min. in 5% sodium thiosulphate, and finally washed for 2 hr. in several changes of distilled water. The samples were dried over silica gel and the loss

in weight, based on the original dry weight of the samples, was found to be 14.9% for the normal wool and 12.2% for the irradiated wool. The difference seems too small to account for the great difference in the progress of the Allworden reaction. Degradation products from the wool which are readily able to diffuse through the epicuticle would play only a small part in the production of Allworden blisters. Possibly irradiation increases the proportion of degradation products of this type.

Since the wool fiber surface is altered by ultraviolet light, new frictional properties are to be expected. Furthermore, Haly et al. [1] suggested that the radiation has an important effect on tyrosine residues in wool, and Earland [2] supported the idea of a correlation between tyrosine modification and antifelting properties of wool. It is likely therefore that irradiated wool has felting properties different from those of normal wool; this aspect is being investigated.

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A. R. HALY

A Submerged Cantilever Densimeter for Fibers

Central Laboratories
N.V. Onderzoekingsinstituut Research
A.K.U. and Affiliated Companies
Arnhem, the Netherlands
November 5, 1957

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

About five years ago the need for a convenient method to measure accurately the density of conditioned fibers was felt in our physical laboratory. A simple hydrostatic balance was devised by H. G. Weijland; it was characterized by a completely submerged weighing system, which obviated the traditionally troubling influence of surface tension on the suspension wire.

The densimeter (Figure 1) consists of a glass vessel, 75 mm. in diameter and 150 mm. in height, with a branch tube at right angles to it. In the branch tube a fused quartz wire (free length 90 mm., diameter 0.2 mm.) is clamped into a bronze plug that is firmly wedged into the tube. The free extremity of the quartz wire extends into the center of the vessel and is so shaped as to form a hook for carrying the sample. The sensitivity of this cantilever wire is about 1 mg./mm. The quartz wire is virtually free from creep and exhibits a remarkable constancy of specific deflection in the course of several years. Owing to its fragility, however, it does not stand rough treatment.

The deflection of the cantilever wire, when loaded, is determined with a precision of 2×10^{-3} mm. by means of a microscope (40 mm. focal length), the height of which is adjustable by means of a screw micrometer.

The glass vessel is filled with an immersion liquid to a level above the branch tube. The liquids used may consist either of a single component or of a mixture of liquids. These liquids should not cause swelling; moreover, their density should be close to that of the fibers. If the sample tends to float it may be weighted down by an auxiliary weight.

For viscose rayon, carbon tetrachloride or a mixture of this liquid with benzene is used.

The advantage of the use of a pure liquid is that, once the density–temperature relation is known, a thermometer will suffice for determining the liquid density. In the case of mixtures, however, the density must be checked frequently because of changes in composition due to evaporation. For this purpose glass floats of calibrated mass and volume are weighed with the cantilever wire in the liquid.

With a view to determining the density of condi-

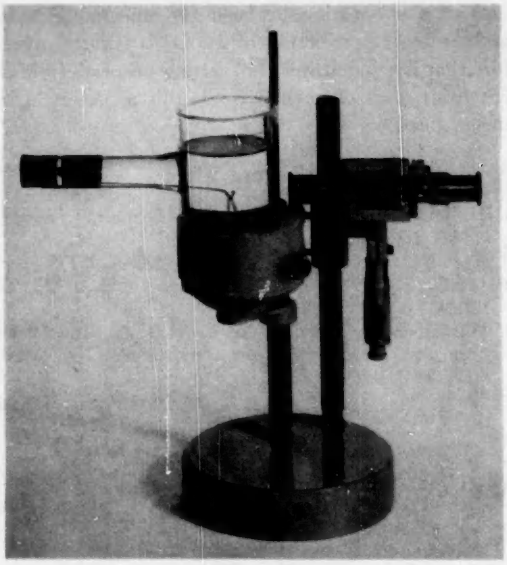

Fig. 1. The submerged cantilever densimeter.

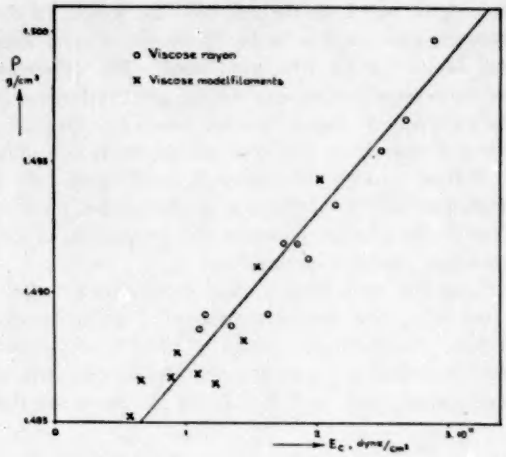

Fig. 2. Relation between density and modulus of dynamic elasticity for conditioned textile viscose rayon yarns and viscose model filaments.

tioned fibers, the immersion liquid should have the proper moisture content. This may be achieved by putting a relatively large quantity of conditioned yarn in the immersion liquid for several days before filling the densimeter vessel.

The yarn sample of about 50 mg. is cleaned with the aid of dichloromethane in a Soxhlet extraction apparatus and subsequently conditioned to a standard atmosphere of 65% R.H. and 20° C. From this sample two 20-mg. skeins are prepared. These skeins are first weighed in air on a torsion balance (correction for buoyancy in air!), then weighed in the densimeter; finally the density of the liquid is determined as indicated above. From these three measurements the density of the fiber sample can be calculated.

Care should be taken that no air bubbles are trapped. Lowering the skein gently into the liquid usually will be effective; highly twisted yarn should be untwisted beforehand.

For the accuracy of the measurement it is necessary that the densimeter should not be subject to vibrations; furthermore, currents in the liquid should be reduced to a minimum. Apart from the currents set up by the introduction of the sample, convection currents arise owing to the evaporation of the liquid at the surface. These are successfully suppressed by covering the vessel with a lid during measurement. In a conditioned room the temperature of the liquid remains sufficiently constant to attain a standard deviation of the density of 3×10^{-4} g./cm^3; for a higher precision the glass vessel should be placed in a thermostat. In general, however, the variability of the yarn samples does not call for this precaution. Duplicate density measurements of a prepared yarn sample take about a quarter of an hour.

One of the subjects this densimeter was used on was an investigation into the relation between density and modulus of dynamic elasticity at 9000 c.p.s. [1] of textile viscose rayon yarns and viscose model filaments (conditioned at 65% R.H., 20° C.). In Figure 2, the density ρ is plotted against the initial value E_c of the modulus of dynamic elasticity. The full line obeys the equation

$$\rho = 1.481 + 6.0 \times 10^{-14} E_c \text{ c.g.s. units}$$

Literature Cited

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